CHAPTER 1

IRON-CATALYZED CROSS-COUPLING REACTIONS

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INTRODUCTION

A cross-coupling reaction[1,2,3] is a fundamental method to create a carbon−carbon bond that has found widespread applications in the synthesis of pharmaceuticals, natural products, optoelectronic materials, polymers, etc. The tremendous impact of this reaction on the scientific community and on society in general is reflected by the Nobel Prize for chemistry being awarded in 2010 to Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki for "palladium-catalyzed cross couplings in organic synthesis."[4] Cross-coupling can be defined as the transition-metal-catalyzed reaction between an organic halide or pseudohalide and an organometallic reagent (Eq. 1).

$$\underset{\substack{\text{organic halide}\\ \text{(or congener)}}}{R^1\text{–}X} \quad + \quad \underset{\substack{\text{organometallic}\\ \text{reagent}}}{R^2\text{–}M} \quad \xrightarrow[\textit{cross-coupling}]{\text{transition-metal catalyst}} \quad R^1\text{–}R^2 \quad + \quad M\text{–}X \qquad \text{(Eq. 1)}$$

Although palladium and nickel catalysts are widely used, the earliest report of a catalytic cross-coupling, which appeared in 1971, used $FeCl_3$ as the catalyst.[5] However, iron was initially largely neglected as a catalyst for cross-coupling, presumably because of the success of other transition metals, especially palladium and nickel, and the difficulties associated with controlling the reactivity of organoiron species. A renaissance of iron catalysis has occurred in recent years, motivated by the perception of the impending scarcity of rare metal elements,[6] as well as by more immediate interests in catalyst cost, availability, toxicity, and environmental friendliness. Moreover, if suitably controlled, iron-catalyzed

reactions can take place much faster than the corresponding reactions catalyzed by heavier metals.[7–12]

Iron is the most common heavy element in the Universe, the main component of the Earth's core, the fourth most common element in the Earth's crust, and is found in all domains of life as an essential component of hemoproteins.[13] The most abundant iron isotope, ^{56}Fe, is one of the most tightly bound nuclei with 8.7903 MeV binding energy per nucleon, being the last nuclide that can be produced exothermically, and therefore gradually building up as the most abundant heavy metal in the Universe.

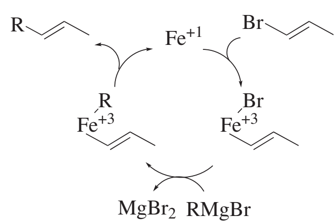
Having 26 protons and hence 26 electrons, the iron atom exhibits a rich chemistry. The organoiron catalyst may, therefore, often be overly reactive and unselective, and the outcome of a catalyzed reaction may be erratic and unpredictable. To make iron catalysis synthetically useful, one must control the oxidation and the spin states of the iron atom as well as the reactivity of the organic component of the system. These challenges are compounded by a lack of mechanistic understanding, mainly because of the difficulties in isolating and characterizing organoiron complexes. Nevertheless, the field of synthetic organic chemistry has witnessed an explosive revival of interest in iron catalysis, and in particular, iron-catalyzed cross-coupling reactions have received much attention recently.

The present review covers the literature on iron-catalyzed cross-coupling reactions from the pioneering work of Kochi in 1971 through 2010. The reactions are grouped according to the type of carbon electrophile and the nature of the carbon nucleophile counterpart. Applications of the method for the synthesis of target compounds are also highlighted. Many reviews on iron catalysis that partially cover this topic have been published.[14–23] The reaction of two organometallic reagents under oxidative conditions[24] and the reaction of two organic halides under reductive conditions are covered in this chapter, but reactions that proceed through carbon–hydrogen bond functionalization,[25,26] reactions with heteroatom nucleophiles,[27] or reactions that involve a carbometalation step[28–34] are not included.

MECHANISM AND STEREOCHEMISTRY

Unlike the mechanisms of palladium- and nickel-catalyzed cross-coupling reactions that have been thoroughly investigated and hence are now well established, the mechanisms of iron-catalyzed cross-coupling reactions are still largely obscure. No consensus has been reached on the nature and the oxidation state of the active species, the catalytic cycle, and the involvement of electron-transfer processes. These problems in part originate from the fact that iron can readily adopt various oxidation and spin states, and that small variations of the reaction conditions may lead to different reactive species and reaction pathways. Moreover, organoiron intermediates are unstable and notoriously difficult to isolate and characterize, further hampering the attempts to obtain mechanistic clues. This section briefly summarizes a few representative mechanistic possibilities, and discusses the mechanisms that have been substantiated with experimental evidence.

Kochi was the first to investigate in detail the iron-catalyzed reaction of alkenyl and alkyl bromides with alkylmagnesium reagents.[35,36] Upon reduction of an Fe(+3) salt with an excess of ethylmagnesium bromide, an intense ESR spectrum was obtained. By comparison with the ESR spectrum of $HFe(dppe)_2$, the authors concluded that the active species is in the Fe(+1) oxidation state. By analogy with the mechanism of palladium- and nickel-catalyzed cross-couplings, an Fe(+1)/Fe(+3) mechanism was proposed, consisting of oxidative addition of the alkenyl bromide to an Fe(+1) species that forms through reduction of the precatalyst with the Grignard reagent, followed by transmetalation and reductive elimination to give the product stereospecifically and to regenerate the iron catalyst (Scheme 1).[35] The oxidative addition of the alkenyl bromide to Fe(+1) is considered to proceed stereospecifically based on analogy with Pd(0) and Ni(0), and is in agreement with the stereospecific cross-coupling of alkenyl bromides. The observed side products, such as diene, alkenylmagnesium bromide, alkene from the alkenyl bromide, and alkene from the alkylmagnesium bromide, are rationalized to arise by the disproportionation of an Fe(+3) species. The reaction rate of the iron-catalyzed cross-coupling of ethylmagnesium bromide with bromoethane was found to be independent of the concentration of organometallic reagent, and approximately first-order dependent on the concentrations of the iron catalyst and the alkyl bromide.[36] This kinetic study suggests that the oxidative addition of an alkyl halide to Fe(+1) is the rate-determining step.

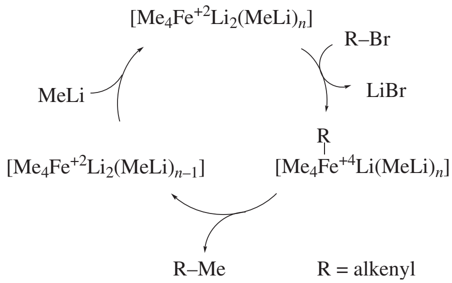


Scheme 1. Iron(+1)/iron(+3) catalytic cycle for the reaction of alkenyl bromides with Grignard reagents.

The Fe(+1)/Fe(+3) mechanism has been revisited recently,[37] and computational analysis has suggested that the reductive elimination step is energetically more favorable for an Fe(+3) species than other lower-valent species. However, species other than Fe(+1) may also be active in the oxidative addition step. Titration experiments to determine the stoichiometry of the initial reduction of iron precatalyst with the organomagnesium reagent were inconclusive, possibly because only part of the iron is reduced to the active form.

On the basis of competition experiments for various substrates in the presence of $FeCl_3$/MeLi at various molar ratios, it is claimed that Fe(+2) “super-ate complexes” are the active species in the reaction of MeLi with alkenyl bromides.[38,39] An Fe(+2)/Fe(+4) catalytic cycle is assumed (Scheme 2),[38] without substantiation of the intermediacy of an Fe(+4) species. The presence of such species is questioned by other authors.[40] Other investigations (discussed below) suggest that

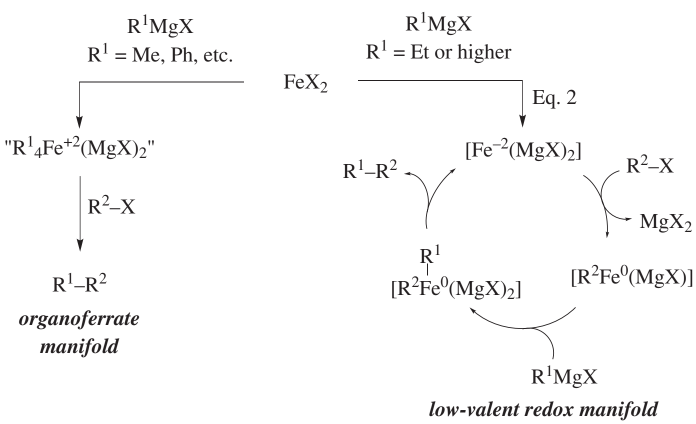
a single-electron-transfer mechanism that involves an Fe(+2)/Fe(+3) catalytic cycle is more reasonable.[41]



Scheme 2. Iron(+2)/iron(+4) catalytic cycle for the reaction of alkenyl bromides with MeLi.

The difference in reactivity between methyl- or arylmagnesium reagents and reagents possessing a β-hydrogen prompted a mechanistic investigation of the iron-catalyzed reaction of Grignard reagents with alkyl halides. Although Grignard reagents that do not possess a β-hydrogen (methyl, phenyl, etc.) may form ferrate complexes,[38,39] use of four equivalents of a Grignard reagent possessing β-hydrogens reduces the precatalyst to produce an Fe(−2) species with the formal composition [Fe(MgX)$_2$], the so-called "inorganic Grignard reagent" (Eq. 2).[42] These nonstabilized, highly reactive, inorganic iron intermediates would then undergo oxidative addition with an alkyl halide to give a formal Fe(0) species, and transmetalation with the organomagnesium reagent and reductive elimination would afford the coupled product and regenerate the active Fe(−2) species (Scheme 3).[43]

$$FeCl_2 + 4\ n\text{-}C_7H_{15}MgBr \longrightarrow \underset{X\,=\,Cl,\ Br}{[Fe(MgX)_2] + 2\ MgX_2 + 2\ (1\text{-}C_7H_{14} + C_7H_{16})} \quad \text{(Eq. 2)}$$

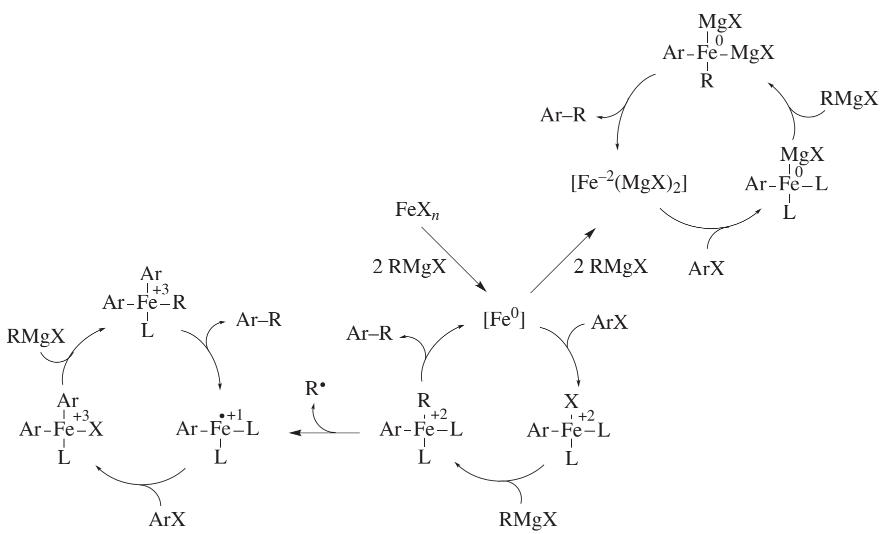


Scheme 3. Organoferrate and low-valent redox manifold for the reaction of alkyl halides with Grignard reagents.

To probe this hypothesis, the isolation of various iron complexes of relevance for the presumed catalytic cycle was carried out.[41] As to the "organoferrate manifold," it was possible to isolate $[(Me_4Fe^{+2})(MeLi)][Li(OEt_2)]_2$, as well as $[Ph_4Fe^0][Li(OEt)_2]$ and its Fe(+2) precursor. These compounds exhibit reactivity similar to that of a catalyst prepared in situ from an iron salt and the corresponding Grignard reagent. As to the "low-valent redox manifold," a structural mimic of $[Fe(MgX)_2]$ has been prepared that matches the reactivity profile of the in situ generated iron species.

Each step of the catalytic cycle was probed using the relevant iron complexes.[41] The low-valent complexes undergo an insertion reaction smoothly with allylic halides and chlorobenzene. As to the high-valent redox manifold, an allyliron(+2) complex react with allyl chloride to give the corresponding allyliron(+3) chloride, suggesting the involvement of a single-electron-transfer process. Finally, an allylphenyliron(+3) complex gives allylbenzene and an Fe(+1) complex at room temperature, demonstrating the feasibility of all of the elementary steps of the proposed iron-catalyzed cross-coupling of an allylic halide with a phenyl anion.

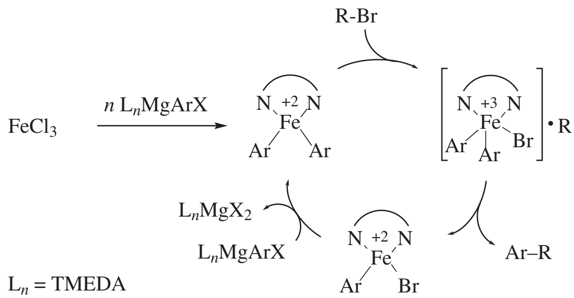
On the basis of these findings, it was concluded that Fe(−2) complexes are the most reactive species to effect the cross-coupling. Besides the Fe(−2)/Fe(0) "low-valent redox manifold," an Fe(0)/Fe(+2) and an Fe(+1)/Fe(+3) competing mechanism may be involved (Scheme 4).[41] Several questions were left open regarding the role of magnesium ions, and the effect of ligands and stabilizing polar solvents, such as N,N,N',N'-tetramethylethylenediamine (TMEDA) or N-methylpyrrolidone (NMP).



Scheme 4. Interconnecting catalytic cycles for the iron-catalyzed cross-coupling reaction.

Insights into the role of the TMEDA ligand have been reported.[44] A diaryliron(+2) complex prepared from a bulky Grignard reagent and TMEDA can be

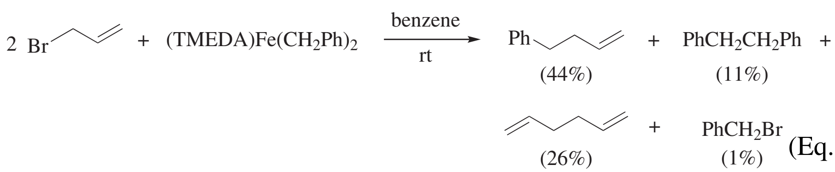
isolated, and is capable of cross-coupling with alkyl halides (Scheme 5).[44] The reaction of this complex with an alkyl chloride is presumed to take place through a single-electron transfer, and a “radical clock experiment” suggests the presence of pathways involving long- and short-lived radicals, controlled by the addition rate of the Grignard reagent and of the diamine ligand.



Scheme 5. Iron(+2)/iron(+3) catalytic cycle for the reaction of alkyl halides with Grignard reagents in the presence of TMEDA.

The involvement of radical pathways in iron-catalyzed cross-coupling reactions has been known for some time. An early investigation showed that a dibenzyliron(+2)/TMEDA complex reacts with a benzyl halide (Eq. 3) or allyl bromide (Eq. 4) at room temperature to give the cross-coupling product.[40] It was argued that radical pathways are involved in these reactions in view of the following observations: (1) scrambling of the deuterium label when the iron complex reacts with 1,1-d_2-allyl bromide, (2) suppression of the coupling reaction when 1,4-cyclohexadiene is used as the reaction solvent, and (3) increased yield of 1,5-hexadiene and an increased amount of benzyl bromide formed when the ratio of allyl bromide/(TMEDA)Fe(CH$_2$Ph)$_2$ is increased.

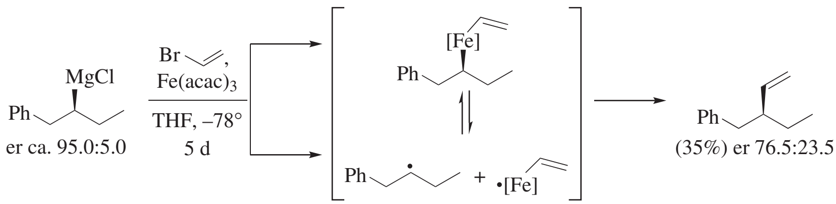
$$\mathrm{PhCH_2X} + \mathrm{(TMEDA)Fe(CH_2Ph)_2} \xrightarrow[\text{rt}]{\text{benzene}} \mathrm{PhCH_2CH_2Ph} \qquad \text{(Eq. 3)}$$



(Eq. 4)

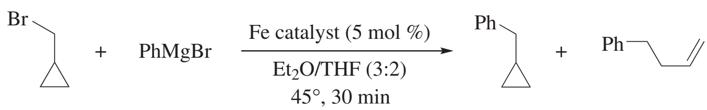
The reaction of an enantiomerically enriched Grignard reagent with vinyl bromide results in significant loss of enantiopurity.[45] This secondary Grignard reagent is known to be configurationally stable under the reaction conditions,[45a] suggesting the loss of enantiopurity is due to a single-electron transfer in the

transmetalation step (Scheme 6),[45] although an alternative mechanism in which transmetalation occurs with retention of configuration is still feasible.



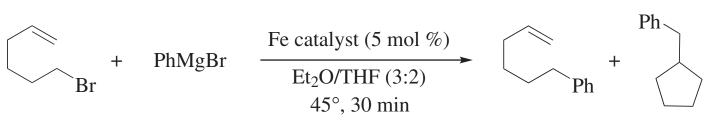
Scheme 6. Single-electron transfer during iron-catalyzed cross-coupling.

Investigation of the electron transfer in the iron/phosphine- or phosphite-catalyzed cross-coupling of an arylmagnesium reagent with an alkyl halide has been reported.[46] Radical-probe experiments suggest that a radical pathway is operative, although the oxidation state of the iron atom remains unclear (Eqs. 5 and 6).[46]



(Eq. 5)

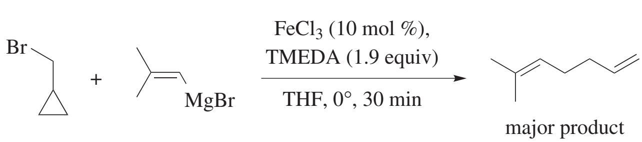
$FeCl_3$ + PCy_3	not detected	(54%)
$FeCl_3$ + $P(O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3)_3$	not detected	(61%)



(Eq. 6)

$FeCl_3$ + PCy_3	(23%)	(40%)
$FeCl_3$ + $P(O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3)_3$	(25%)	(42%)

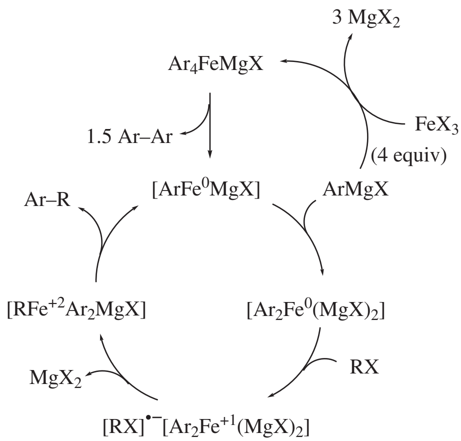
A radical clock probe has also been employed to explore the involvement of radical pathways in the iron-catalyzed cross-coupling of an alkyl halide with an alkenylmagnesium reagent (Eq. 7).[47] The nature of the active species was not discussed, although it was hypothesized that the oxidative addition step proceeds through a single-electron-transfer mechanism.



(Eq. 7)

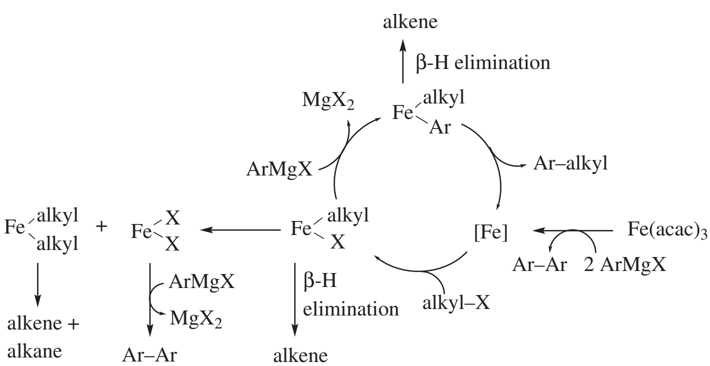
An Fe(0)/Fe(+2) mechanism in which the oxidative addition of an alkyl halide to ferrate(0) species proceeds through two single-electron-transfer processes was

proposed for the cross-coupling of arylmagnesium reagents with alkyl halides (Scheme 7).[48] A ferrate(0) complex, $[Ar_2Fe(MgX)_2]$, formed by reduction of $Fe(acac)_3$ by an arylmagnesium reagent, first undergoes single-electron transfer to an alkyl halide to generate $[RX]^{\bullet-}$ $[Ar_2Fe^{+1}(MgX)_2]$. After formation of $R^{\bullet}$ and X^{-} from $[RX]^{\bullet-}$, Fe−R bond formation takes place through a formal single-electron transfer to form $[RFe^{+2}Ar_2MgX]$, which undergoes reductive elimination of Ar−R to regenerate the ferrate(0) catalyst. However, this scenario was not substantiated by experiments, except by the fact that the reaction is less sensitive to steric effects than a similar palladium-catalyzed reaction.



Scheme 7. Two successive single-electron-transfer steps.

A mechanism that involves a two-electron oxidative addition process rather than a single-electron transfer was also proposed for a similar reaction (Scheme 8),[49] without being substantiated by experimental evidence. The



Scheme 8. Two-electron oxidative addition mechanism.

catalytically active iron species [Fe] formed in situ undergoes oxidative addition of alkyl–X to produce alkyl–Fe–X. After formation of alkyl–Fe–Ar via transmetalation with ArMgX, reductive elimination occurs to afford the coupled product, alkyl–Ar, and to regenerate the catalyst, [Fe]. The authors rationalized the formation of the byproducts through a disproportionation event after the oxidative addition.

In conclusion, despite numerous efforts, there is at present no unified view about the mechanisms of iron-catalyzed cross-coupling reactions. Some of the proposed mechanisms appear to be feasible; however, it is likely that small modifications of the reaction parameters lead to significant changes in the mechanism because of the high sensitivity of the spin states of iron to the coordination environment of the metal. Moreover, competing reaction manifolds may be involved, and trace quantities of other metals in iron catalysts, particularly copper and palladium, may significantly affect the outcome of the reactions.[49a,50] These issues further complicate the mechanistic picture. Taking these problems into account, general mechanistic principles for the iron-catalyzed cross-coupling are impossible to draw unequivocally. The mechanistic studies performed to date seem to suggest a few general guidelines:

(1) The active species: when the organometallic reagent does not possess a β-hydrogen and in the absence of a ligand, iron-ate complexes are plausible candidates. When the organometallic reagent does possess a β-hydrogen, a low-valent species may form. Although Fe(+1) complexes were originally considered to be the most probable active species, recent evidence suggests that Fe(−2) complexes are the most reactive. When a ligand such as TMEDA is present, there is evidence that Fe(+2) complexes may be the active species, at least when arylmagnesium reagents are used as the nucleophilic partner.
(2) When low-valent iron species are involved, they are reactive enough for oxidative addition of an organic halide to proceed. An Fe(+2) species, on the other hand, may undergo a single-electron transfer to an organic halide.
(3) Different mechanistic cycles may be interconnected, and different mechanisms may also compete depending on the specific reaction conditions.

Regarding stereochemistry, the iron-catalyzed cross-coupling of alkenyl halides or pseudohalides with organometallic reagents generally takes place with retention of the configuration of the double bond, but depending on the substrate and reaction conditions, partial isomerization may also occur. For example, the reaction of alkenyl halides with a methylmagnesium halide in THF takes place stereospecifically, but when higher alkylmagnesium halides are used, the configurational homogeneity is not preserved.[5,51,52,35] The reaction of an (*E*)-alkenyl halide takes place stereospecifically, whereas a (*Z*)-alkenyl halide may lead to partial isomerization.[53] However, upon addition of an excess amount of

NMP, the reactions take place stereospecifically in most cases, regardless of the type of alkylmagnesium reagent employed.[54]

The reaction of an alkenylmagnesium halide[55,47] or an alkenylzinc reagent[56] with an alkyl halide proceeds with retention of the double bond geometry. Oxidative homocoupling of alkenylmagnesium compounds also proceeds stereospecifically.[57]

Alkenyl phosphates[58] and sulfones[59] react with alkylmagnesium reagents with retention of configuration, but partial isomerization occurs when arylmagnesium compounds are used.[58] The reaction of α-chloroenynes with alkylmagnesium reagents occurs without loss of isomeric purity.[60] Desulfinylative coupling of (*E*)-2-phenylethenesulfonyl chloride with aryl- and alkylmagnesium reagents proceeds with complete retention of the double bond configuration.[61] In contrast to these stereospecific reactions, alkenyl pivalates react with alkylmagnesium reagents with isomerization of the double bond, presumably because of the involvement of radical species.[58]

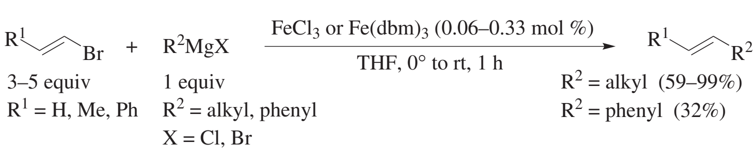
The reaction of an (*E*)- or (*Z*)-alkenyl chloride with an alkylmanganese compound proceeds stereospecifically.[62,63] The reaction of an (*E*)-alkenyl iodide with a terminal alkyne also takes place with retention of configuration.[64]

Iron-catalyzed cross-couplings involving an enantiomerically enriched partner often give racemic products, which strongly suggests the involvement of radical species. For example, significant loss of enantiopurity is observed in the reaction of an enantiomerically-enriched Grignard reagent with vinyl bromide.[45] However, the enantiopurity is preserved if the stereogenic atom is far from the reaction center.[65] The reaction of an enantiomerically enriched alkyl halide with an arylmagnesium reagent proceeds with loss of enantiomeric purity.[66] By contrast, the iron-catalyzed reaction of an enantiomerically enriched allylic carbonate with a malonate anion proceeds with a high degree of retention of configuration at the stereogenic center.[48]

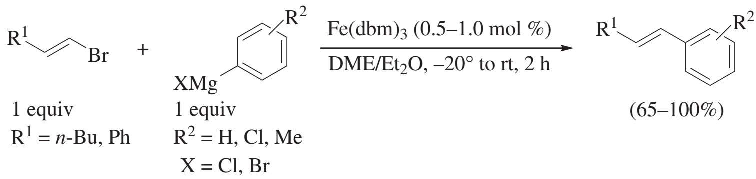
SCOPE AND LIMITATIONS

Cross-Coupling Reactions of Alkenyl Electrophiles

Reactions with Organomagnesium Compounds. The cross-coupling reaction of alkenyl bromides with alkylmagnesium reagents takes place smoothly at ambient temperature in THF in the presence of $FeCl_3$,[5,51] $Fe(dbm)_3$,[52,35] or other iron salts (Eq. 8).[52] Three to five equivalents of an alkenyl bromide are necessary to achieve synthetically viable product yields. The reaction with a phenylmagnesium reagent gives a poor yield (32%) under the same conditions.[52] However, the reaction of an alkenyl halide with an arylmagnesium reagent is consistently high-yielding in DME and Et_2O, even when one equivalent of an alkenyl bromide is used (Eq. 9).[53]

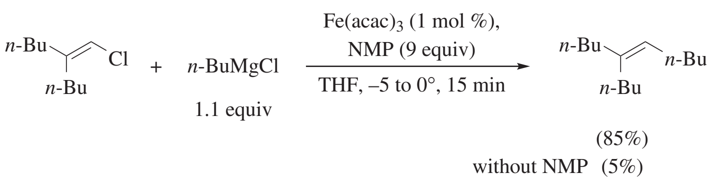


(Eq. 8)

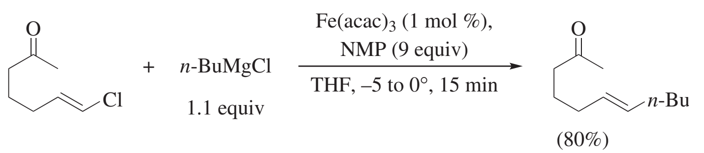


(Eq. 9)

Addition of an excess amount of NMP dramatically improves the yield of the cross-coupling reaction of an alkenyl halide with an alkylmagnesium reagent. For instance, the reaction of 2-*n*-butyl-1-chlorohexene with *n*-butylmagnesium chloride affords 5-*n*-butyl-5-decene in 85% yield in the presence of nine equivalents of NMP, whereas only a 5% yield is obtained in the absence of the polar additive (Eq. 10).[54] Functional groups such as ester and ketone carbonyls remain intact (Eq. 11).[54]

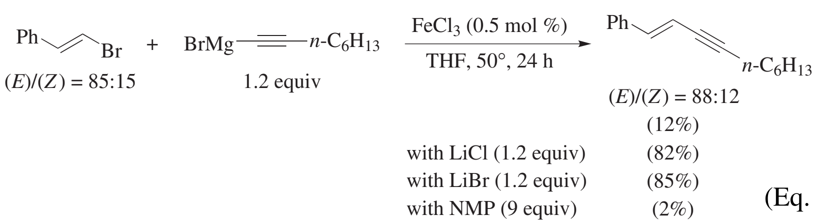


(Eq. 10)

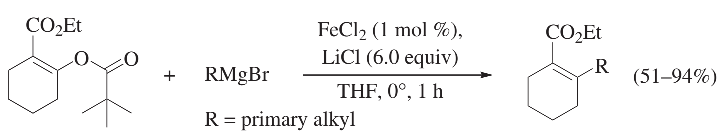


(Eq. 11)

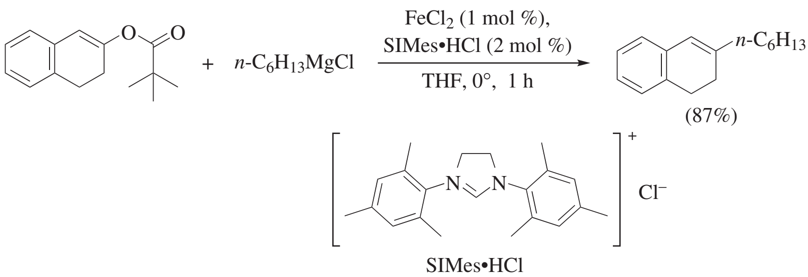
Addition of a stoichiometric amount of LiCl or LiBr is very effective for the coupling reaction of alkenyl bromides with alkynylmagnesium reagents, for which NMP is not at all effective (Eq. 12).[67] Similarly, alkenyl pivalates, known to be less reactive than alkenyl halides and sulfonates, react with alkylmagnesium reagents in the presence of an excess of LiCl (Eq. 13).[68] Addition of a catalytic amount of the *N*-heterocyclic carbene (NHC) ligand precursor SIMes•HCl gives comparable results in the absence of LiCl (Eq. 14).[68]



(Eq. 12)

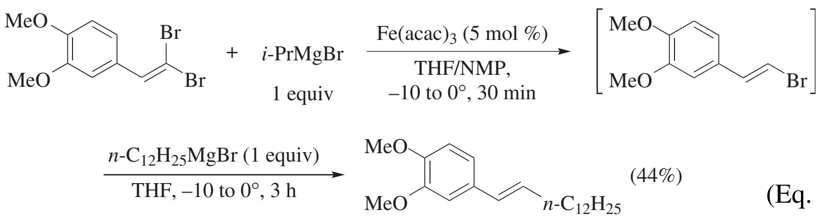


(Eq. 13)



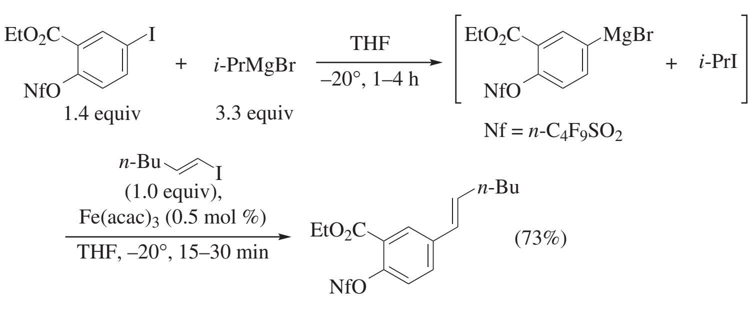
(Eq. 14)

4-(2,2-Dibromovinyl)-1,2-dimethoxybenzene reacts sequentially with 2-propylmagnesium bromide and *n*-dodecylmagnesium bromide to give (*E*)-1,2-dimethoxy-4-(tetradec-1-enyl)benzene via stereoselective hydrodebromination and cross-coupling reactions (Eq. 15).[69] The reaction with two equivalents of *n*-dodecylmagnesium bromide gives the same product in 45% yield.



(Eq. 15)

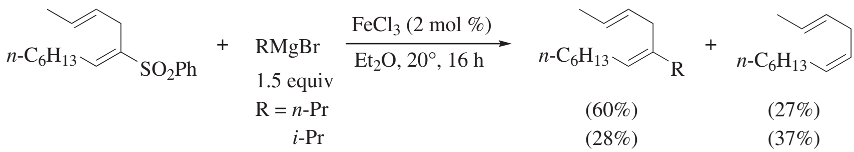
Arylmagnesium reagents, prepared from the corresponding aryl iodides and 2-propylmagnesium bromide, react with alkenyl iodides in the presence of $Fe(acac)_3$ (Eq. 16).[70] Styrene derivatives possessing ester, cyano, and sulfonyl groups can be prepared in a stereospecific manner.



(Eq. 16)

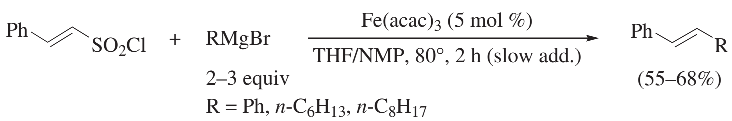
In the presence of $FeCl_3$, an alkenyl sulfone reacts with *n*-propylmagnesium to give the coupling product in moderate yield, along with a significant amount of reduction product (Eq. 17).[59] On the other hand, the reaction with 2-propylmagnesium bromide produces predominantly the reduction product, probably

because of the formation of an iron hydride species via rapid β-hydride elimination from the secondary alkyl group.



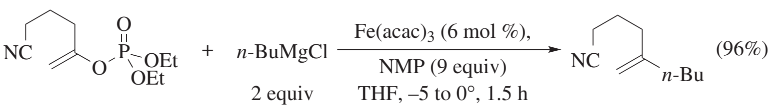
(Eq. 17)

Desulfinylative coupling is successful with the use of a catalytic amount of $Fe(acac)_3$ and an excess of NMP. Thus, (*E*)-2-phenylethenesulfonyl chloride reacts with aryl and alkylmagnesium reagents to afford (*E*)-styrene derivatives with complete retention of the double bond configuration (Eq. 18).[61] The reaction in the presence of a palladium catalyst instead of $Fe(acac)_3$ does not give the desired desulfinylative coupling product, but rather oxidative homocoupling products of the Grignard reagent.[71]

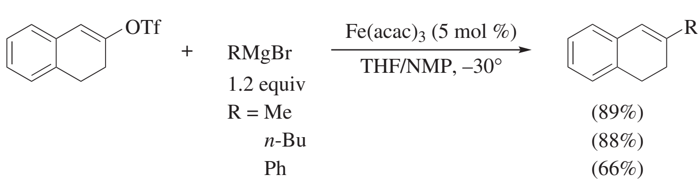


(Eq. 18)

Enol phosphates[54,72] and sulfonates,[73] readily prepared from the corresponding carbonyl compounds, also serve as electrophiles in the presence of $Fe(acac)_3$ and NMP (Eqs. 19[72] and 20[73]). The reaction takes place smoothly at low temperature, and thus a variety of functional groups remain intact.



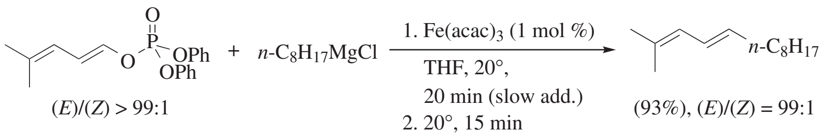
(Eq. 19)



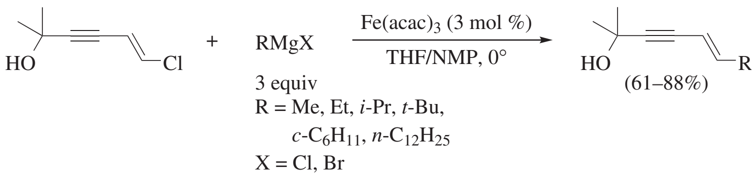
(Eq. 20)

Dienol phosphates react with primary and secondary alkylmagnesium reagents to afford the corresponding coupling products in good to excellent yields (Eq. 21).[58] Slow addition of the Grignard reagent at 20° is important to achieve high yields. The coupling reaction of a terminal dienol phosphate takes place in a highly stereoretentive manner. Arylmagnesium reagents also take part in the reaction, but cause partial isomerization of the double bond. The reaction of

chloroenynes with three equivalents of an alkylmagnesium reagent in the presence of NMP occurs in good yield without loss of isomeric purity (Eq. 22).[60]

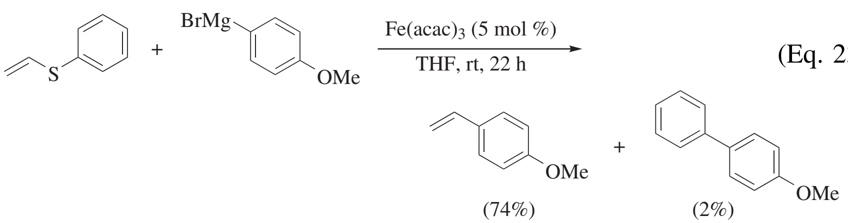


(Eq. 21)



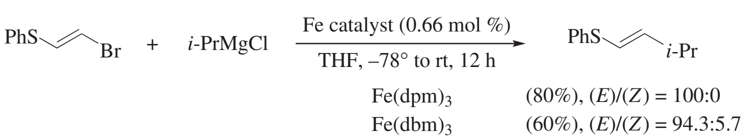
(Eq. 22)

Alkenyl sulfides serve as a good electrophile for this coupling process. Alkenyl carbon–sulfur bond cleavage prevails over aryl carbon–sulfur bond cleavage; the reaction of phenyl vinyl sulfide with 4-methoxyphenylmagnesium bromide gives 4-methoxystyrene and 4-methoxybiphenyl in 74% and 2% yields, respectively (Eq. 23).[74] This result is in sharp contrast to the conventional palladium- and nickel-catalyzed processes, where both alkenyl carbon–sulfur and aryl carbon–sulfur bonds undergo cross-coupling with electrophiles.[75]



(Eq. 23)

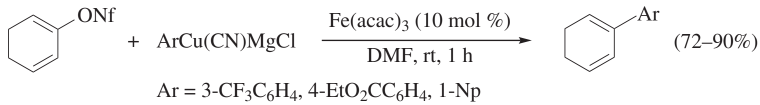
(E)-(2-Bromoethenyl)thiobenzene bearing two potential leaving groups reacts with 2-propylmagnesium chloride via selective carbon–bromine cleavage to afford (E)-(3-methylbut-1-enyl)phenylsulfide as the sole product (Eq. 24).[76] $Fe(dpm)_3$ is the best catalyst in terms of yield and stereoselectivity.



(Eq. 24)

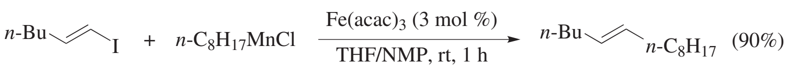
Reactions with Organocopper Compounds. Gilman-type cyanocuprates, prepared from the corresponding arylmagnesium reagents and CuCN•LiCl, react with enol and dienol sulfonates in the presence of $Fe(acac)_3$ to afford the coupling products in good yields (Eq. 25).[77] The coupling reaction can proceed in the

absence of an iron catalyst, albeit in low yield. Ester, cyano, trifluoromethyl, and bromo substituents are compatible with the reaction conditions.

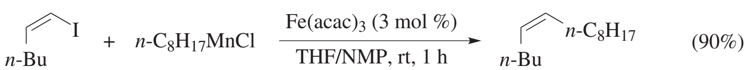


(Eq. 25)

Reactions with Organomanganese Compounds. Organomanganese compounds can also be coupled with alkenyl electrophiles. Preparation of the organomanganese reagent is achieved by simple mixing of an organomagnesium or organolithium compound with a manganese(+2) halide, or by direct insertion of activated Mn(0) into the corresponding organic halide. This coupling reaction has a broader substrate scope than that using Grignard reagents: aryl and *n*- or *sec*-alkylmanganese chlorides react smoothly with alkenyl chlorides, bromides, and iodides in a highly chemoselective and stereospecific manner (Eqs. 26a and 26b).[62,63]

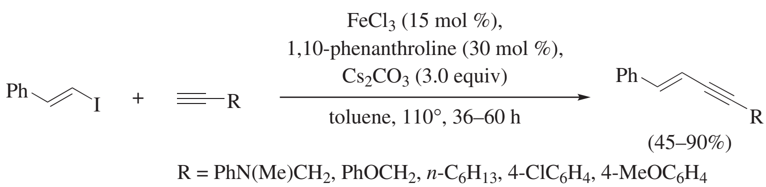


(Eq. 26a)



(Eq. 26b)

Reactions with Miscellaneous Nucleophilic Compounds. In the presence of 1,10-phenanthroline, $FeCl_3$ catalyzes the Sonogashira-like cross-coupling of alkenyl iodides with terminal alkynes (Eq. 27).[64] Other diamine ligands, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and *N*,*N*′-dimethylethylenediamine (DMEDA) also give coupling products, but in lower yields. Aryl- and alkyl-substituted terminal alkynes possessing *N*-methyl-*N*-phenylamino, methoxy, phenoxy, and chloro substituents react well. Whereas a variety of alkenyl iodides give moderate to good yields, alkenyl bromides do not afford any coupling products under these reaction conditions, which represents a significant limitation of this iron-catalyzed reaction.[78]

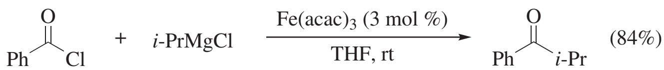


(Eq. 27)

Cross-Coupling Reactions of Acyl Electrophiles

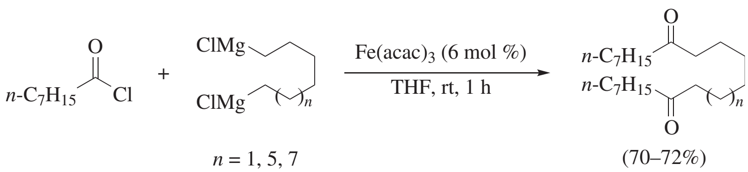
Reactions with Organomagnesium Compounds. The cross-coupling reaction of acyl chlorides with organomagnesium compounds takes place smoothly

in the presence of a catalytic amount of $Fe(acac)_3$ (Eq. 28[79]).[73,80–82] The reaction has several synthetically attractive features, such as high yield, chemoselectivity, and no need for precious transition metals and ligands. Therefore, this reaction is suitable for the large-scale production of ketones.



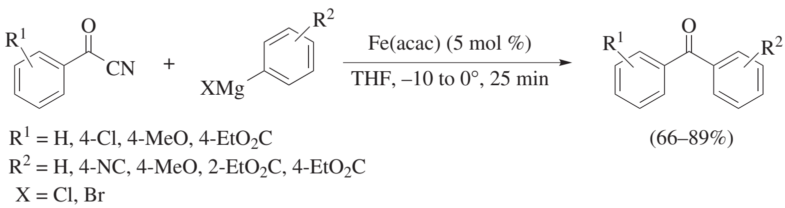
(Eq. 28)

Double acylation of an organodimagnesium compound can be achieved in the presence of 6 mol % of $Fe(acac)_3$ (Eq. 29).[81] *S*-Phenyl carbonochloridothioate participates in the coupling reaction to give the corresponding dicarboxylic thiol esters in good yields.



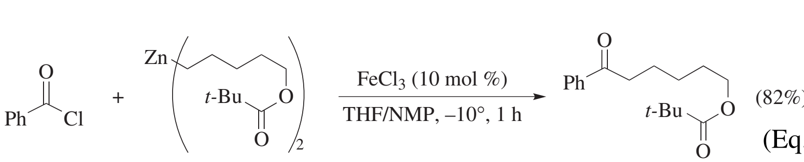
(Eq. 29)

The reaction of an arylmagnesium reagent with an acyl cyanide takes place smoothly at −10 to 0° to afford benzophenone derivatives in good yields, whereas the reaction with benzoyl chloride gives lower yields (38–53%) (Eq. 30).[83] A variety of functional groups such as chloro, methoxy, cyano, and ethoxycarbonyl remain intact under the reaction conditions.



(Eq. 30)

Reactions with Organozinc Compounds. The reaction of an acyl chloride with an alkylzinc compound takes place in the presence of 10 mol % of $FeCl_3$ and excess NMP (Eq. 31).[84] The coupling product can be obtained in slightly higher yields in the presence of $CoBr_2$ instead of $FeCl_3$.[84]

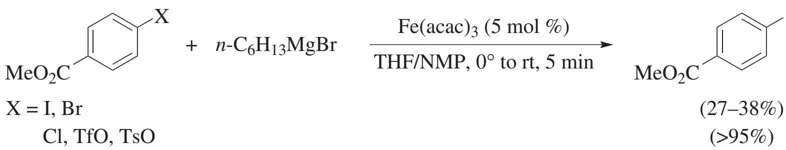


(Eq. 31)

Cross-Coupling Reactions of Aryl Electrophiles

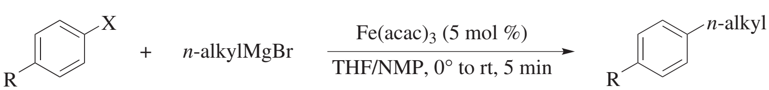
Reactions with Organomagnesium Compounds. The cross-coupling reactions of an aryl and heteroaryl chloride, triflate, tosylate, and phosphate with

an alkylmagnesium reagent proceed smoothly in the presence of $Fe(acac)_3$ or $FeCl_3$ and an excess of NMP as a cosolvent.[85–89,43,73,49] The reaction of an aryl chloride, triflate, or tosylate with *n*-hexylmagnesium bromide leads to almost quantitative formation of the desired alkylbenzoic acid ester, whereas the corresponding aryl bromide or iodide provides less satisfactory yields (Eq. 32).[85] This observation is in sharp contrast to the conventional nickel and palladium catalysts, wherein aryl bromides and iodides provide the coupling products equally in good yields.[90,91]



(Eq. 32)

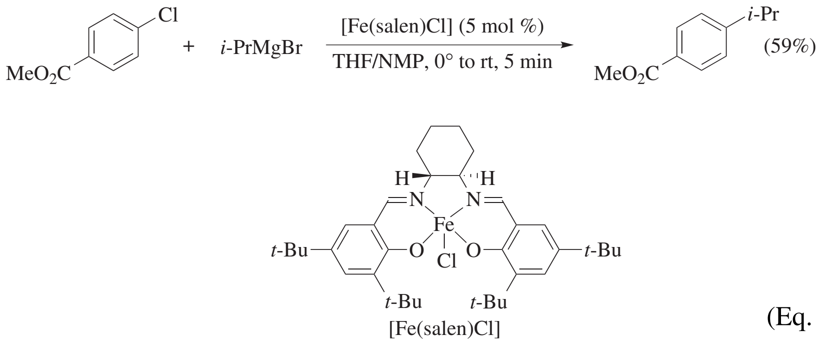
Because conditions for reaction with an alkylmagnesium reagent are mild and selective (with complete reaction in a few minutes at or below ambient temperature), various functional groups such as esters, nitriles, sulfonates, sulfonamides, thioethers, acetals, alkynes, and trifluoromethyl groups are well tolerated. Many heterocyclic electrophiles can be used, such as pyridine, pyrimidine, triazine, quinoline, isoquinoline, carbazole, purine, pyridazine, pyrazine, quinoxaline, quinazoline, uracil, thiophene, and benzothiazole derivatives.[43] Although electron-deficient aryl chlorides, triflates, and tosylates give the desired coupling products in good to excellent yields (Eq. 33),[85] the scope of the reaction is rather narrow.



R	X	Yield (%)
MeO_2C, NC, CF_3, *i*-$PrOSO_2$, (*i*-$Pr)_2NSO_2$	Cl, TfO, TsO	72–94
Me	Cl, TsO	0
Me	TfO	81

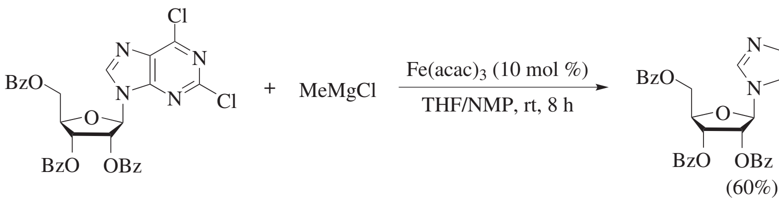
(Eq. 33)

In stark contrast to the high reactivity of primary alkylmagnesium reagents, secondary alkyl-, allyl-, and alkenylmagnesium reagents provide poor to moderate results in the presence of $Fe(acac)_3$ and NMP. However, secondary alkylmagnesium reagents do react with electron-deficient aryl chlorides to give the desired coupling products in moderate yields by using an [Fe(salen)Cl] complex as the precatalyst (Eq. 34).[43]



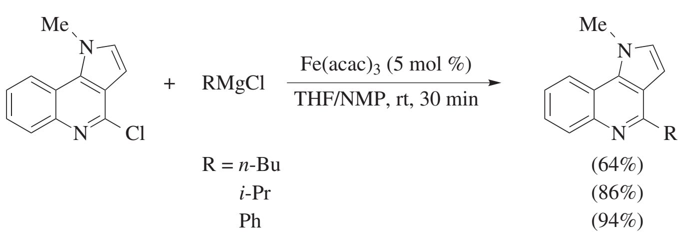
(Eq. 34)

The reaction of benzoyl-protected 2,6-dichloropurine riboside with one equivalent of methylmagnesium chloride site-selectively affords the desired 6-methylated product in 60% yield (Eq. 35).[86] This reaction can be performed with protected purine bases and with acyl-protected ribosides and 2-deoxyribosides. After deprotection, various free purine bases and nucleosides are obtained in good to excellent yields.



(Eq. 35)

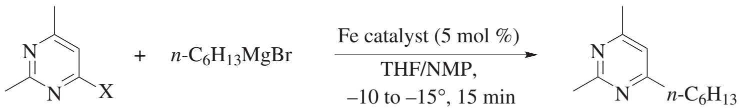
In the case of heteroaromatic substrates, not only primary alkyl- but also secondary alkylmagnesium or phenylmagnesium reagents smoothly take part in the cross-coupling reaction.[88] The cross-coupling reaction of 4-chloro-1-methyl-1*H*-pyrrolo[3,2-*c*]quinoline with alkyl- and arylmagnesium reagents in the presence of $Fe(acac)_3$ and NMP affords novel pyrrolo[3,2-*c*]quinoline derivatives in good to high yields (Eq. 36).[88]



(Eq. 36)

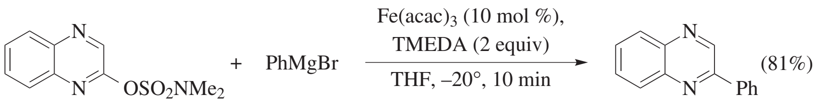
Heteroaromatic tosylates, phosphates, and sulfamates are also suitable electrophiles in iron-catalyzed cross-coupling reactions with Grignard reagents (Eqs. 37 and 38).[89] Moreover, pivalates and carbamates are good leaving groups.[68] The reaction of 2-naphthyl pivalate proceeds in moderate yield, but

the yield is dramatically improved by the use of a more stable carbamate, which has rarely been utilized as an electrophile in such a process (Eq. 39).[68]

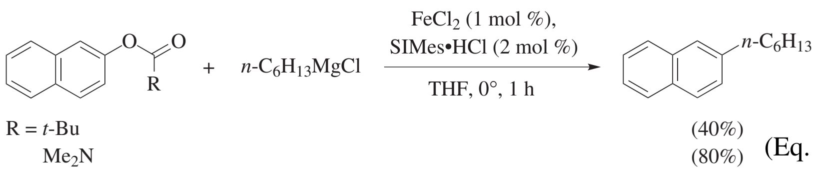


(Eq. 37)

X	Catalyst	Yield (%)
TsO	$Fe(acac)_3$	98
$(EtO)_2PO_2$	$FeCl_3$	88

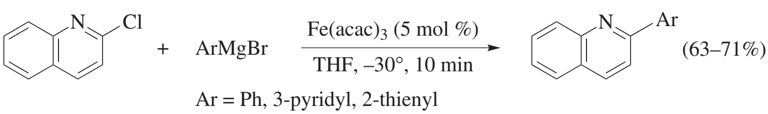


(Eq. 38)



(Eq. 39)

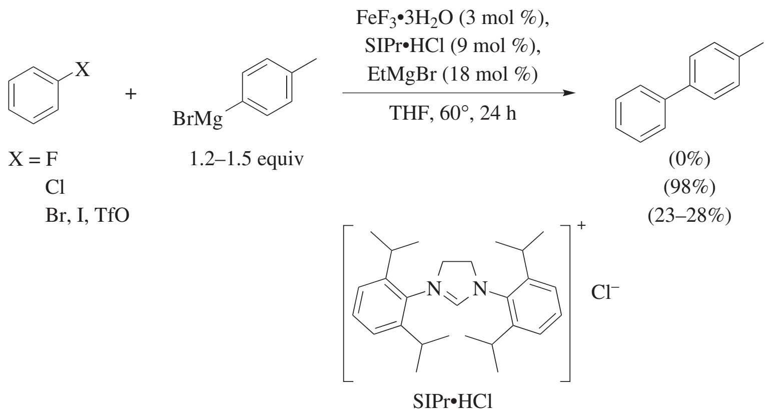
In the presence of $Fe(acac)_3$ or [Fe(salen)Cl], a π-electron-deficient heterocycle can be coupled with an arylmagnesium or heteroarylmagnesium reagent to give the corresponding biaryl product in moderate to good yield (Eq. 40).[43,92] On the other hand, the reactions of electron-rich aryl halides with arylmagnesium reagents tend to fail because of competing homocoupling reactions.



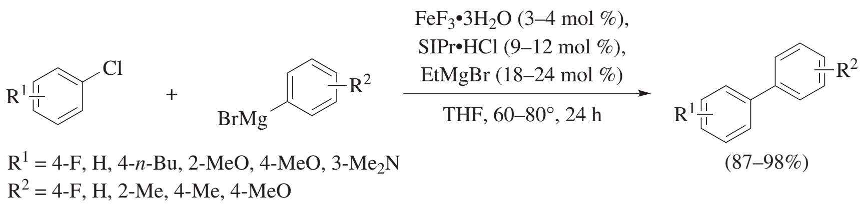
(Eq. 40)

In contrast to the modest results obtained when $Fe(acac)_3$ or [Fe(salen)Cl] are used as the catalyst, the combination of iron fluoride with an NHC ligand gives the desired biaryl cross-coupling product in excellent yields and selectivity.[93] A variety of aryl- and heteroarylmagnesium reagents couple selectively and efficiently with electron-deficient aryl halides such as π-electron-deficient heterocycles, and also with electron-rich aryl chlorides. Although bromo- and iodobenzene, and phenyl triflate lead to poor results, chlorobenzene reacts with 4-tolylmagnesium bromide to afford the desired biaryl cross-coupling product selectively, together with a negligible amount of biphenyl and a small amount of 4,4′-dimethylbiphenyl (Eq. 41).[93] A carbon–fluorine bond is entirely inert under the reaction conditions (Eq. 41). An increase in reaction temperature allows a 2-substituted aryl chloride to react with 2-substituted arylmagnesium reagents or 1-naphthylmagnesium reagent and provides sterically hindered biaryl products in high yields (Eq. 42).[93,94] The origin of the unique catalytic effect

of the fluoride counterion can be ascribed to the formation of a higher-valent heteroleptic metalate ($[ArFeF_2]MgBr$) as the key intermediate in the proposed catalytic cycle.[94] Note that other catalyst systems, such as $Cp(PMe_2Ph)_2FeBr$[95] and $FeCl_3$ with a stoichiometric amount of TMEDA,[47] are not applicable to the biaryl-forming coupling reaction.

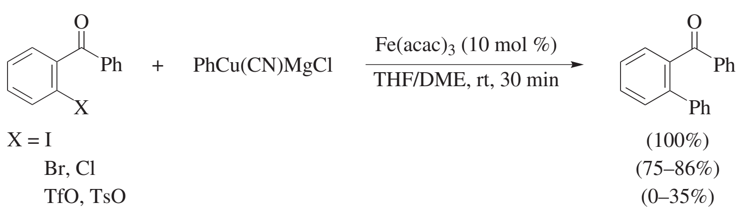


(Eq. 41)

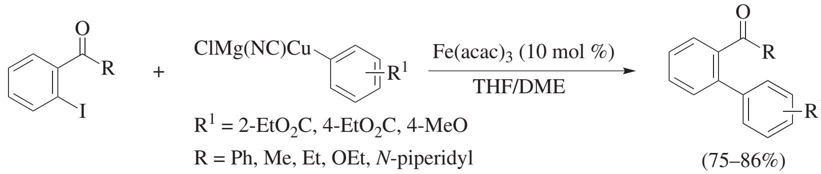


(Eq. 42)

Reactions with Organocopper Compounds. Gilman-type cyanocuprates, prepared from the corresponding arylmagnesium reagents and CuCN•LiCl, are good nucleophiles for selective cross-coupling rather than homocoupling, and show useful functional-group compatibility.[96] Aryl iodides are the best electrophiles, bromides and chlorides exhibit moderate reactivity, and triflates and tosylates react very poorly (or not at all) (Eq. 43).[96] Amine, amide, nitrile, ester, and ketone groups on the electrophile are tolerated. Remarkably, a methyl ketone such as 2-iodoacetophenone, undergoes iron-catalyzed cross-coupling without any competitive deprotonation of the methyl ketone or addition to the carbonyl group. Organocopper compounds possessing an amine, alkoxy, triflate, acetal, nitrile, or ester group can be used (Eq. 44).[96] Heteroarylcopper compounds are also suitable reagents for this cross-coupling reaction.

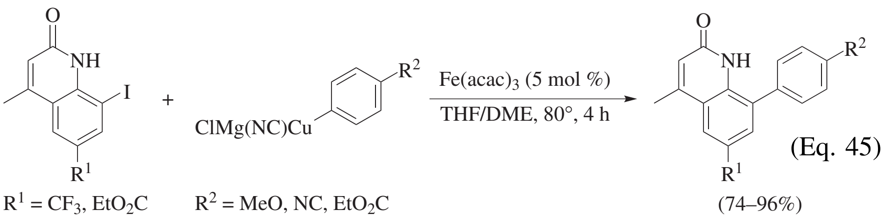


(Eq. 43)

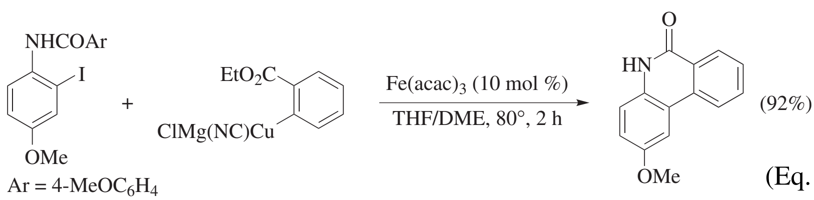


(Eq. 44)

The iron-catalyzed cross-coupling reaction between a functionalized arylcopper compound and an aromatic iodide bearing an amide or an unprotected 2-quinolinone moiety leads smoothly to polyfunctionalized biaryls in excellent yields (Eq. 45).[97] Using 2-carbethoxyphenylcopper as the nucleophile, one can achieve intramolecular cyclization with the amide to obtain phenanthridinone derivatives in good yield (Eq. 46).[97]

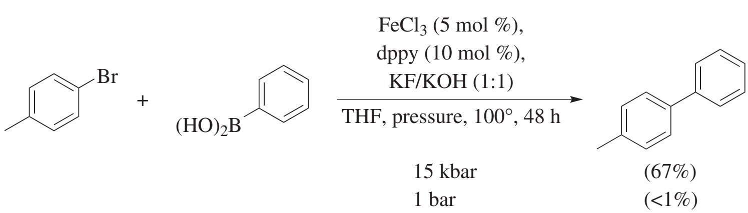


(Eq. 45)



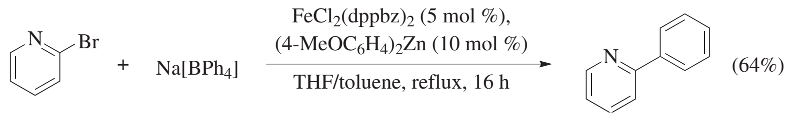
(Eq. 46)

Reactions with Organoboron Compounds. The Suzuki–Miyaura cross-coupling reaction of an aryl bromide with a phenylboronic acid proceeds in the presence of $FeCl_3$ as the catalyst under high pressure (15 kbar) conditions (Eq. 47).[98] It is usually difficult to reduce iron(+3) to a low-valent state with phenylboronic acid, and therefore the authors suggest that the influence of pressure on the iron-catalyzed reaction may accelerate the reduction of the iron(+3) to a catalytically active oxidation state, although no experimental evidence was presented.



(Eq. 47)

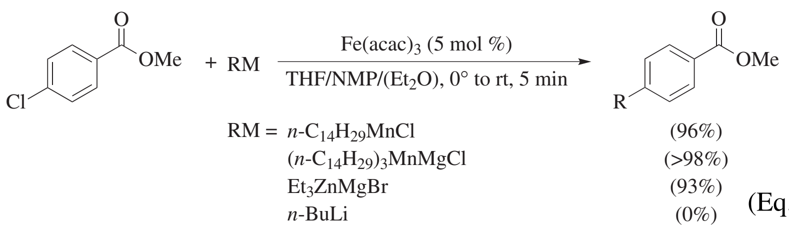
The Suzuki–Miyaura cross-coupling reaction of a 2-haloheteroarene with sodium tetraphenylborate is catalyzed by $FeCl_2(dppbz)_2$ (dppbz = 1,2-bis(diphenylphosphino)benzene), with the aid of 10 mol % of the zinc compound $(4\text{-}MeOC_6H_4)_2Zn$ (Eq. 48).[99] Use of a phenylboronic acid or its pinacol ester instead of sodium tetraphenylborate did not give any coupling product. It was suggested that an in situ prepared arylzinc compound plays a key role in the transmetalation between the arylboron compound and the iron catalyst.[100]



(Eq. 48)

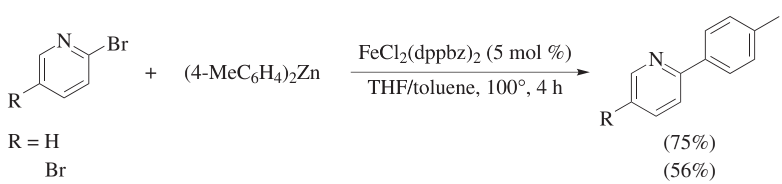
Although iron-catalyzed biaryl formation using an arylboronic acid as a nucleophile has been reported twice,[101,102] both papers were retracted[103,104] after additional experimental verification was performed.[105]

Reactions with Miscellaneous Nucleophilic Compounds. In the presence of $Fe(acac)_3$ and NMP as the cosolvent, methyl 4-chlorobenzoate reacts with an organomanganese reagent or trialkylzincate to give an alkylated product in high yield.[85,43] However, the use of n-BuLi or Et_3Al fails to afford any cross-coupling product (Eq. 49).[85,43] An iron-ate complex, such as Me_3FeLi or $[(Me_4Fe)(MeLi)][Li(OEt_2)]_2$, can react with aryl chlorides and iodides in low to moderate yields in the absence of any catalyst and additive.[106,107,41]



(Eq. 49)

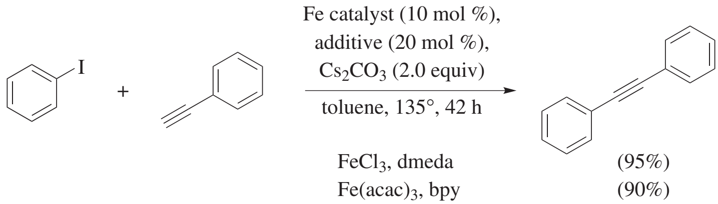
The iron-catalyzed Negishi coupling reaction of a 2-haloheteroarene with a diarylzinc compound has also been reported.[99] The precatalyst, $FeCl_2(dppbz)_2$, catalyzes the site-selective reaction at the pyridine 2-position to afford the biaryl compounds in moderate yields (Eq. 50).[99]



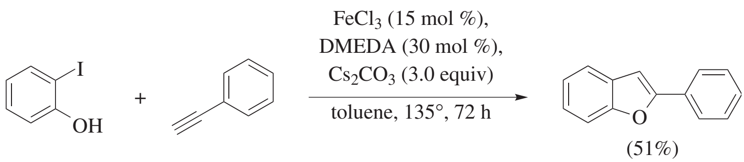
(Eq. 50)

The combination of $FeCl_3$ and DMEDA,[108] or $Fe(acac)_3$ and 2,2′-bipyridine (bpy),[109] catalyzes the Sonogashira-like coupling reaction of an aryl or heteroaryl

iodide with a terminal alkyne (Eq. 51). Whereas aryl and heteroaryl iodides bearing amine, methoxy, chloro, or fluoro groups show good reactivity, aryl bromides, chlorides, fluorides, and tosylates are inert under the reaction conditions. Aryl, alkyl, and triethylsilylacetylenes are viable nucleophiles. The reaction of 2-iodophenol with an aryl acetylene gives a 2-arylbenzofuran in moderate yields via Sonogashira-like coupling followed by cyclization (Eq. 52).[108]



(Eq. 51)

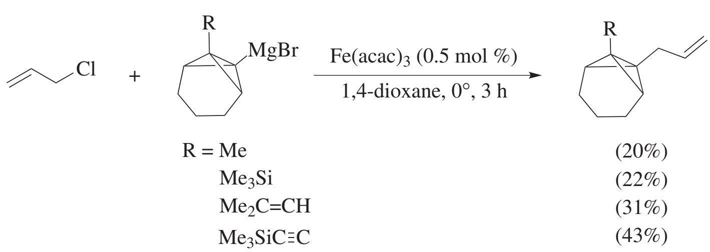


(Eq. 52)

Cross-Coupling Reactions of Allylic, Propargylic, and Benzylic Electrophiles

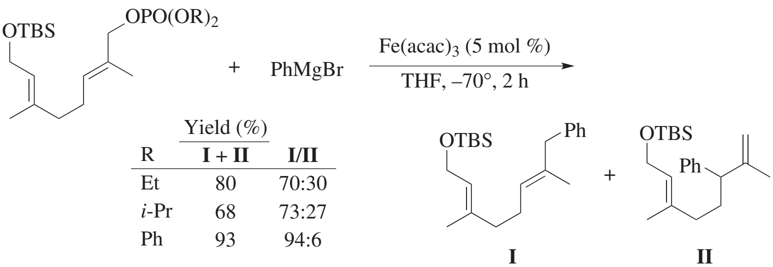
Allylation of Organomagnesium Compounds. Although the cross-coupling reaction of an allylic electrophile with a Grignard reagent in the absence of a transition metal catalyst can proceed, the reaction rate, yield, and selectivity are usually unsatisfactory.[109a] Some alternative methods for cross-coupling with an organomagnesium reagent using iron catalysis have been reported: $Fe(acac)_3$ is used for the reaction of allylic chlorides,[110] allylic phosphates,[111,112] and 2-alkenesulfonyl chlorides;[113] $FeCl_3$ is used for the reaction of allylic bromides;[36] and $[Li(TMEDA)]_2[Fe(C_2H_4)_4]$ is used for the reaction of allylic chlorides and bromides.[114,41]

In the presence of 0.5 mol % of $Fe(acac)_3$, tricyclo[4.1.0.0^{2,7}]hept-1-ylmagnesium reagents (prepared from the corresponding alkyl bromides, *n*-BuLi, and $MgBr_2$) react with an allylic halide or a propargylic halide at 0° to afford the corresponding coupling product (Eq. 53).[110] The reaction affords only traces of coupling product in the absence of the iron catalyst.



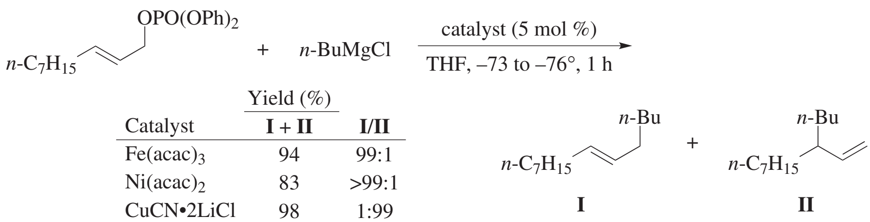
(Eq. 53)

Allylic phosphates can be used as electrophiles for the iron-catalyzed cross-coupling reaction with Grignard reagents. A diphenylphosphate is superior to a diethyl or diisopropylphosphate as a leaving group for S_N2-selective cross-coupling reactions (Eq. 54).[111] Primary and secondary alkyl-, alkenyl-, alkynyl-, and phenylmagnesium reagents afford the corresponding coupling products in 54–95% yields with high S_N2-selectivities, in which the double bond configuration is retained. In the absence of the iron catalyst, the reaction does not proceed, even at 0°. Nearly exclusive S_N2-selectivities are obtained using $Fe(acac)_3$ and $Ni(acac)_2$, whereas high S_N2'-selectivities are observed when CuCN•2LiCl is used as a catalyst (Eq. 55).[112]



	Yield (%)	
R	I + II	I/II
Et	80	70:30
i-Pr	68	73:27
Ph	93	94:6

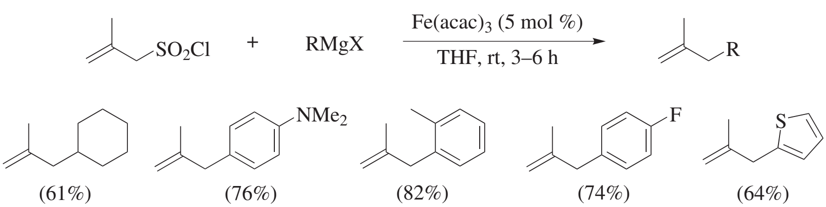
(Eq. 54)



	Yield (%)	
Catalyst	I + II	I/II
$Fe(acac)_3$	94	99:1
$Ni(acac)_2$	83	>99:1
CuCN•2LiCl	98	1:99

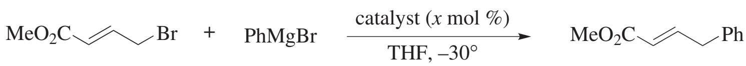
(Eq. 55)

Allylic sulfonyl chlorides, prepared from the corresponding alkene and sulfur dioxide through a BCl_3-promoted ene reaction, can be used as electrophilic partners in an iron-catalyzed desulfinylative cross-coupling reaction with various organomagnesium reagents (aromatic, aliphatic, and heteroaromatic) (Eq. 56).[113] The reaction tolerates a wide range of functional groups, including carbonyl groups that are prone to react quickly with an organomagnesium reagent. As was also found for the desulfinylative carbon–carbon bond-forming reaction of an alkyl- or alkenylsulfonyl chloride with an organomagnesium reagent,[61] $Fe(acac)_3$ in THF appears to be a better catalyst than $FeCl_3$.



(Eq. 56)

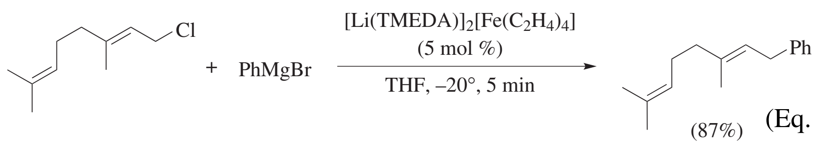
The catalytic activity of various structurally defined, preformed iron complexes has been investigated for the cross-coupling reaction of methyl 4-bromocrotonate with phenylmagnesium bromide (Eq. 57).[41] Although all complexes are catalytically potent, their efficiencies are strikingly different. The Fe(−2) species $[Li(TMEDA)]_2[Fe(C_2H_4)_4]$ outperforms, in terms of yield and reaction rate, all other catalysts bearing an iron center with a higher formal oxidation state (0, +1, +2, and +3).



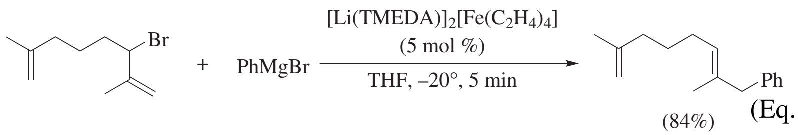
Catalyst	x	Time (min)	Yield (%)
$[Li(TMEDA)]_2[Fe^{-2}(C_2H_4)_4]$	5	<10	94
$[Li(TMEDA)][CpFe^{0}(C_2H_4)_2]$	5	30	45
$Cp^*Fe^{+1}(C_2H_4)_2$	10	30	50
$(cyclooctenyl)CpFe^{+2}(C_2H_4)$	10	30	46
$(allyl)Cp^*Fe^{+3}Cl$	10	30	73

(Eq. 57)

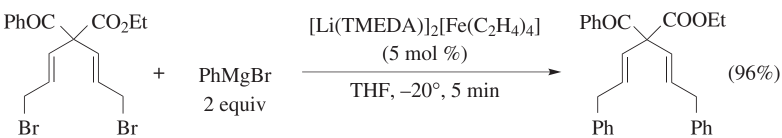
The aryl moiety of phenylmagnesium bromide is introduced site-selectively at the least hindered site of the allylic system in the presence of a low-valent iron complex, $[Li(TMEDA)]_2[Fe(C_2H_4)_4]$ (Eqs. 58 and 59).[114,41] Ketone, ester, and silyl groups remain intact under these reaction conditions (Eq. 60).[114,41]



(Eq. 58)

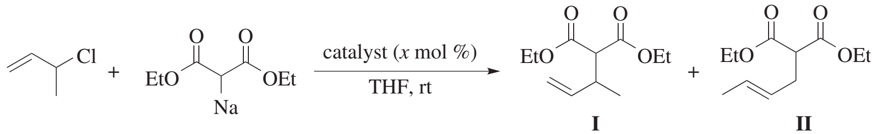


(Eq. 59)



(Eq. 60)

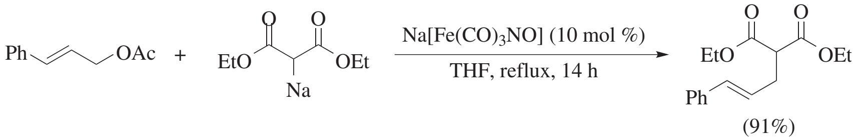
Allylation of Active Methylene Compounds. Alkylation of allylic substrates such as chlorides, acetates, and formates with diethyl malonate anion is catalyzed by the iron complexes $(\eta^3\text{-crotyl})Fe(CO)_2NO$ and $Na[Fe(CO)_3NO]$ (Eq. 61).[115] The reaction of cinnamyl acetate takes place in a highly S_N2-selective manner to give diethyl 2-cinnamylmalonate as the sole product (Eq. 62).[115]



Catalyst	x	Time (h)	Yield (%) I + II	I/II
(η^3-crotyl)$Fe(CO)_2NO$	10	0.4	84	74:26
$Na[Fe(CO)_3NO]$	20	48	90	82:18[a]

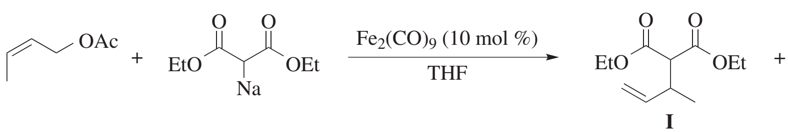
[a] Originally reported as 82:28.[52]

(Eq. 61)

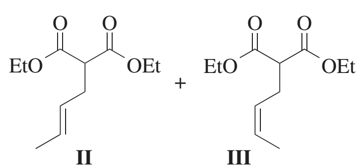


(Eq. 62)

Diiron nonacarbonyl promotes the cross-coupling of an allylic acetate with a malonate anion in good yield (Eq. 63).[116,117] The site- and stereoselectivity of transition-metal-catalyzed allylations is well known to be substrate, nucleophile, catalyst, and solvent dependent.[118] In this reaction system, the site selectivity is low to modest and is temperature dependent. Stereoselective substitution with retention of olefin configuration can be achieved, but requires a lower reaction temperature in the case of (*Z*)-2-butenyl acetate (Eq. 63).



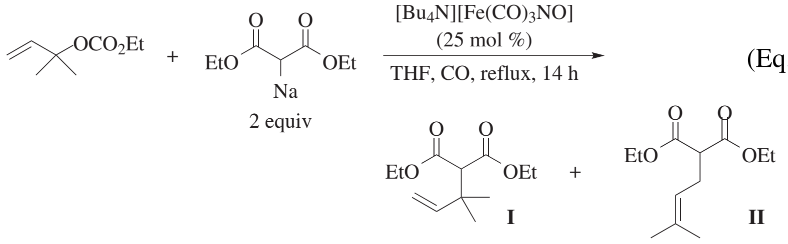
Temp (°)	Time	Yield (%) I + II + III	I/II/III
66	24 h	84	41:59:0
20	4 d	78	69:0:31



(Eq. 63)

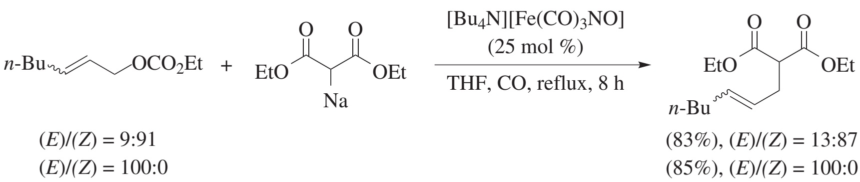
The catalyst tetrabutylammonium (tricarbonylnitrosyl)ferrate, $[Bu_4N][Fe(CO)_3NO]$,[119–122] is easier to prepare and less sensitive to air and moisture than the corresponding sodium derivative $Na[Fe(CO)_3NO]$.[115] In the presence of $[Bu_4N][Fe(CO)_3(NO)]$, alkylation of allylic carbonates with malonate anions occurs predominantly at the carbon atom to which the leaving group is attached, even in the case of a tertiary substrate (Eq. 64).[122] No significant isomerization of the double bond is observed even at elevated temperature (Eq. 65).[122] The retention of configuration suggests that this reaction may not proceed via a π-allyl

complex but rather via a σ-allyl complex, because it is known that isomerization of the double bond commonly takes places in π-allylpalladium complex mediated allylation reactions.[123] The reaction of an enantiomerically enriched allylic carbonate with malonate anion proceeds with high retention of configuration at the stereogenic center (Eq. 66).[48] This selectivity is often observed in palladium-catalyzed allylic alkylation reactions as well.[118]

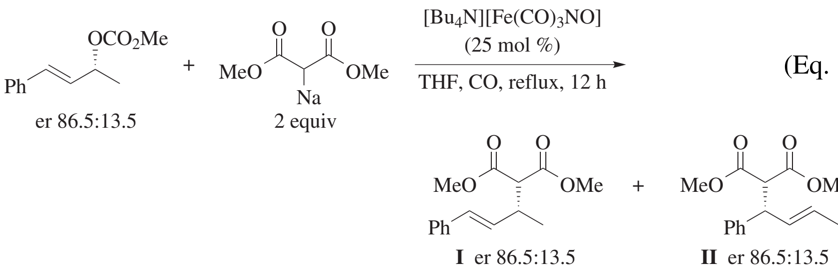


(Eq. 64)

I + **II** (78%), **I**/**II** = 92:8



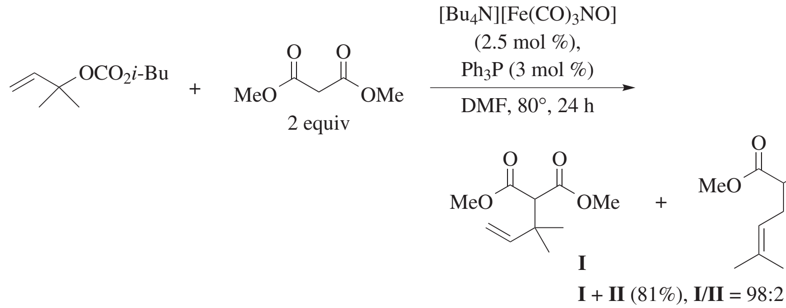
(Eq. 65)



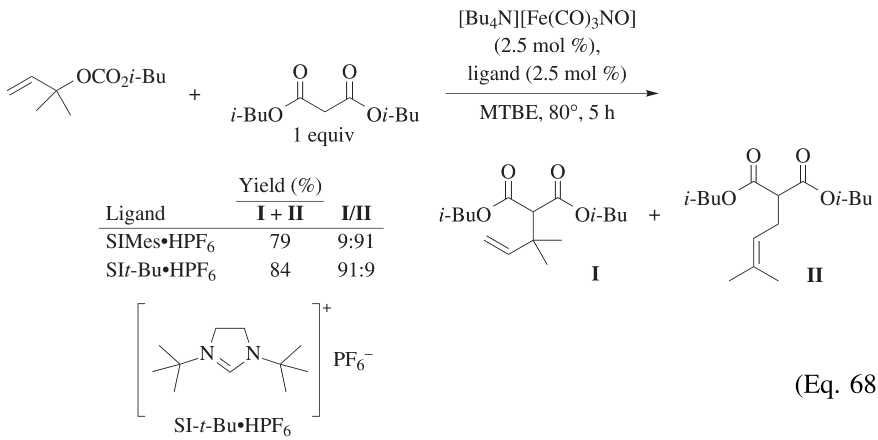
(Eq. 66)

I + **II** (78%), **I**/**II** = 93:7

Two modified reaction conditions for the $[Bu_4N][Fe(CO)_3NO]$ catalyzed allylation reaction of malonates have been reported. Efficient iron-catalyzed allylation with an allylic carbonate proceeds with low catalyst loading (2.5 mol %) in the presence of triphenylphosphine as the ligand and DMF as the solvent (Eq. 67).[120] Furthermore, the pronucleophile does not need to be deprotonated in a separate step, and utilization of the toxic carbon monoxide atmosphere is avoided. Inversion of the site selectivity as compared with the original reaction is observed when SIMes•HPF_6 is used as the ligand, leading to predominant formation of the S_N2' addition product (Eq. 68).[121] The use of the more sterically hindered ligand SI-*t*-Bu•HPF_6, bearing *tert*-butyl groups at the nitrogen atoms, leads to the S_N2 addition product with high selectivity. Ester, ketone, nitrile, and sulfonyl groups on the active methylene compound are tolerated.



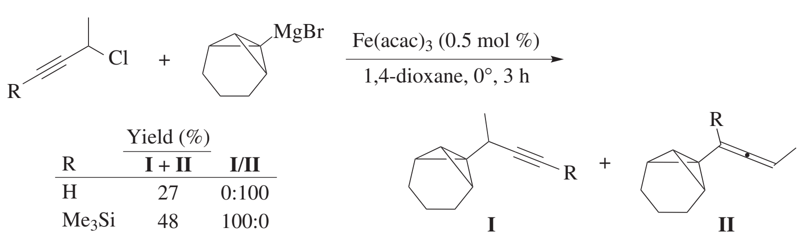
(Eq. 67)



Ligand	Yield (%) I + II	I/II
SIMes•HPF$_6$	79	9:91
SI*t*-Bu•HPF$_6$	84	91:9

(Eq. 68)

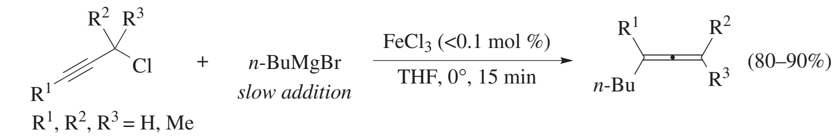
Propargylation of Organomagnesium Compounds. Although the cross-coupling of Grignard reagents with a propargylic halide in the absence of a suitable catalyst gives a low yield, the reaction proceeds smoothly in the presence of 0.5 mol % of Fe(acac)$_3$.[110] The coupling reaction of tricyclo[4.1.0.0^{2,7}]hept-1-ylmagnesium bromide with secondary propargylic halides possessing a terminal alkyne gives the allene products selectively, albeit in poor yield (Eq. 69).[110] If the terminal alkyne carbon carries a trimethylsilyl group, alkyne products are formed. This selectivity is in contrast to the results obtained in the copper-mediated reaction of related terminally substituted propargylic compounds that afford S$_N$2′ addition products.[124,125]



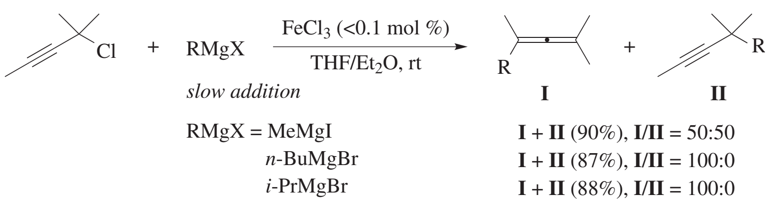
R	Yield (%) I + II	I/II
H	27	0:100
Me$_3$Si	48	100:0

(Eq. 69)

In the presence of a trace amount of $FeCl_3$ (<0.1 mol %), terminal primary, secondary, tertiary, and nonterminal tertiary propargylic chlorides react with primary or secondary alkylmagnesium reagents (added slowly to the reaction mixture) to produce allene products in good to excellent yields (Eq. 70).[126,127] Whereas primary and secondary alkylmagnesium reagents give allene products selectively, methylmagnesium iodide gives a 1:1 mixture of allene and alkyne products (Eq. 71).[127] Cobalt, nickel, and copper salts can also be used as catalysts for this reaction if the organomagnesium reagents are added very slowly.

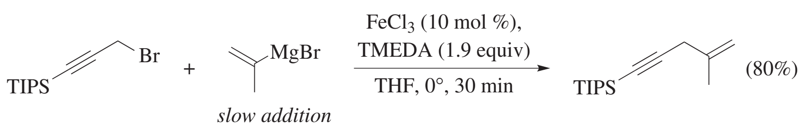


(Eq. 70)

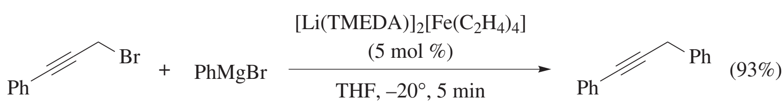


(Eq. 71)

The cross-coupling reaction of a propargylic electrophile with an aryl- or alkenylmagnesium reagent proceeds in the presence of $FeCl_3$ and TMEDA (Eq. 72),[47] or low-valent iron complex $[Li(TMEDA)]_2[Fe(C_2H_4)_4]$ (Eq. 73).[114,41] In these reactions, propargylic coupling products are the major products, with only small amounts of allenic side products.



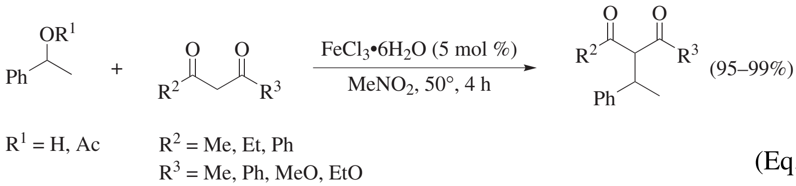
(Eq. 72)



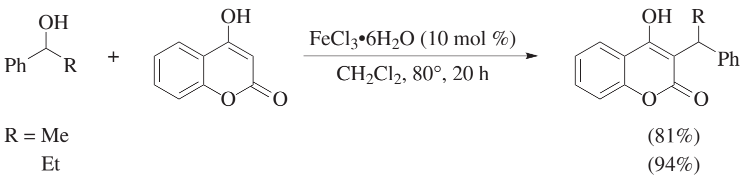
(Eq. 73)

Benzylation of Miscellaneous Nucleophilic Compounds. Various acidic 1,3-dicarbonyl compounds and methyl 3-acetamidobut-2-enoate react with benzylic alcohols or acetates in the presence of $FeCl_3{\bullet}6H_2O$ to give the corresponding 2-benzylated products in good to excellent yields (Eq. 74).[128] Benzyl alcohol, its acetate and carbonate, afford only low yields because of the decreased stability of the corresponding carbocation intermediate compared to 1-phenylethyl electrophiles; but the more electron-rich 4-methoxy-substituted benzyl alcohol reacts

in higher yield. Using this method, bioactive 4-hydroxy-3-(1-phenylalkyl)-2*H*-chromen-2-ones can be synthesized from 4-hydroxycoumarin and 1-phenylethyl or 1-phenylpropyl alcohols (Eq. 75).[128]

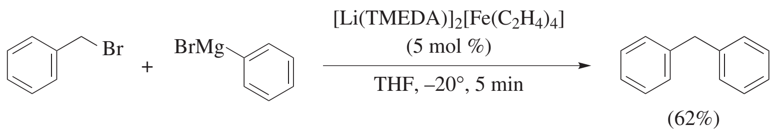


(Eq. 74)

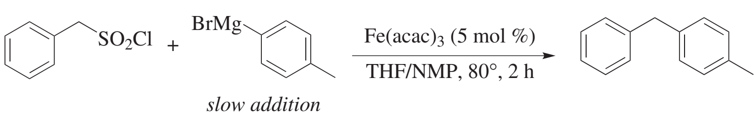


(Eq. 75)

Benzylic halides undergo cross-coupling with organomagnesium reagents in the presence of a catalytic amount of $FeCl_3$,[36] $FeCl_2$•H_2O and PMe_2Ph,[95] or low-valent iron complex $[Li(TMEDA)]_2[Fe(C_2H_4)_4]$ (Eq. 76).[41] The desulfinylative cross-coupling reaction of benzyl sulfonyl chloride with an arylmagnesium reagent is accomplished by using a catalytic amount of $Fe(acac)_3$ and excess NMP (Eq. 77).[61]



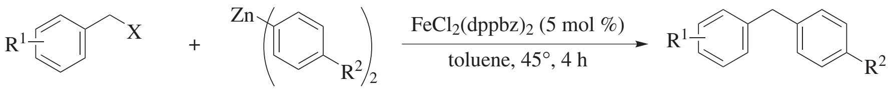
(Eq. 76)



(Eq. 77)

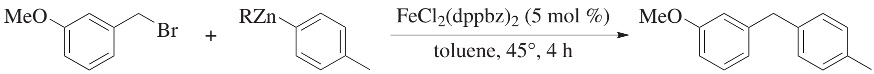
Arylzinc compounds undergo iron-catalyzed cross-coupling reactions with benzyl halides and phosphates.[129] The preformed iron complex, $FeCl_2(dppbz)_2$, shows excellent activity and selectivity. The reaction tolerates electron-donating and -withdrawing groups on both the benzylic substrate and the diarylzinc compound, as well as sensitive functional groups such as ester and nitrile on the benzylic halide (Eq. 78).[129] A bromine substituent on the aromatic ring of the benzylic electrophiles is tolerated under the reaction conditions. This observation is noteworthy as this selectivity cannot be achieved using nickel or palladium catalysis because of competitive arylation of the aryl bromide fragments.[130] The low activity of ArZnX and the transfer of only one aryl group from the Ar_2Zn species is a disadvantage when employing more complex or expensive aryl groups. However, trimethylsilylmethyl or *N*,*N*-dimethylbenzylamino groups can

be used as a nontransferable ligand, and the desired cross-coupling product is obtained selectively in good yields (Eq. 79).[129]



R^1 = 4-MeO, 4-Me, 4-Br, 2-CF$_3$, 2-NC, 4-MeO$_2$C (73–99%)
X = Cl, Br, (EtO)$_2$PO$_2$
R^2 = MeO, Me, CF$_3$

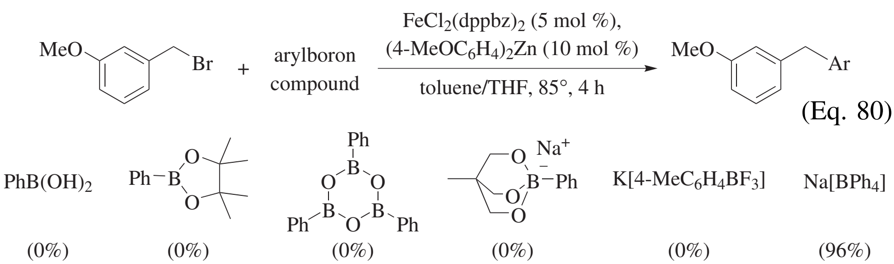
(Eq. 78)



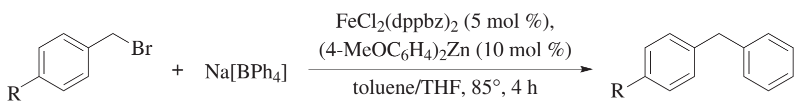
R = Me$_3$SiCH$_2$ (74%)
2-(Me$_2$NCH$_2$)C$_6$H$_4$ (89%)

(Eq. 79)

The preformed iron complex FeCl$_2$(dppbz)$_2$ also catalyzes Suzuki–Miyaura cross-coupling reactions of benzyl halides with tetraarylborate salts in the presence of 10 mol % of the zinc compound (4-MeOC$_6$H$_4$)$_2$Zn (Eq. 80).[99] The reaction does not proceed with phenylboronic acid or its pinacol ester in place of sodium tetraphenylborate (Eq. 80).[99] Apart from the nitro group, other functional groups on the benzyl halide substrates, such as cyano, ester, trifluoromethyl, and bromide are well tolerated (Eq. 81).[99] Benzyl chlorides show slightly lower reactivity, but benzyl phosphates are poor substrates.



(Eq. 80)



(Eq. 81)

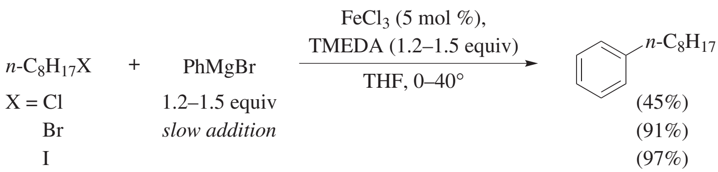
R = Me, Br, CF$_3$, MeO$_2$C (90–99%)
R = O$_2$N (0%)

Cross-Coupling Reactions of Alkyl Electrophiles

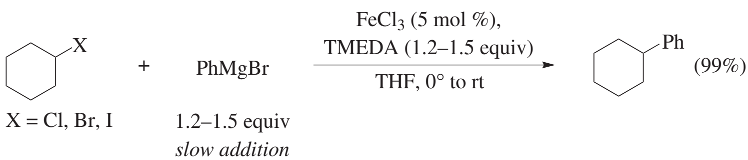
Recent progress in iron catalysis has made it possible to efficiently cross-couple alkyl electrophiles possessing β-hydrogens with organometallic compounds in the presence of certain iron salts or complexes. This section

summarizes the scope and limitations of iron-catalyzed cross-coupling reactions of unactivated alkyl electrophiles with various nucleophiles.

Reactions with Organomagnesium Compounds. Tetramethylethylenediamine is one of the most widely used additives for iron-catalyzed cross-coupling of alkyl halides with organomagnesium compounds.[66,114,131,48,55,47,41] In the presence of a stoichiometric amount of TMEDA, primary alkyl bromides and iodides react with phenylmagnesium bromide to afford the coupling products in high yields, whereas primary alkyl chlorides give moderate yields (Eq. 82).[66] Secondary alkyl halides such as cyclohexyl halides show higher reactivity than primary alkyl halides, affording the cross-coupling products in higher yields (Eq. 83).[66] In regard to the aryl nucleophile, electron-rich aryl Grignard reagents react rapidly, whereas reagents with an electron-withdrawing group react sluggishly.

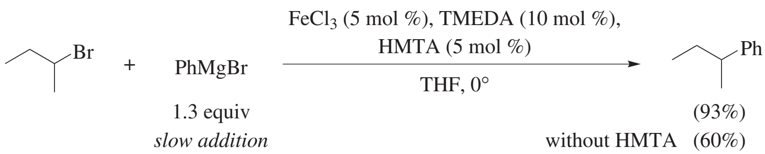


(Eq. 82)

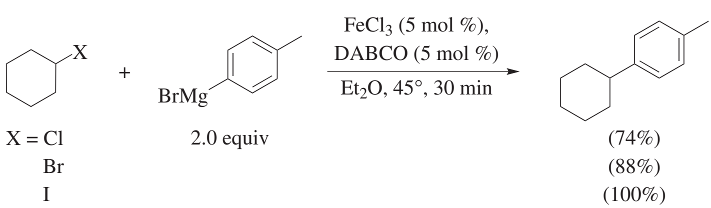


(Eq. 83)

Although the use of a substoichiometric amount of TMEDA decreases the yield of $FeCl_3$-catalyzed cross-coupling reactions,[131,48] the combined use of TMEDA and hexamethylenetetramine (HMTA) as additives is found to improve the yield of the coupling product (Eq. 84).[48] In addition to TMEDA, other simple amines such as Et_3N or DABCO also effect the cross-coupling reaction of alkyl halides in diethyl ether at elevated temperature (Eq. 85).[131] These catalytic systems are applicable to cross-coupling reactions of primary and secondary alkyl chlorides, bromides, and iodides.

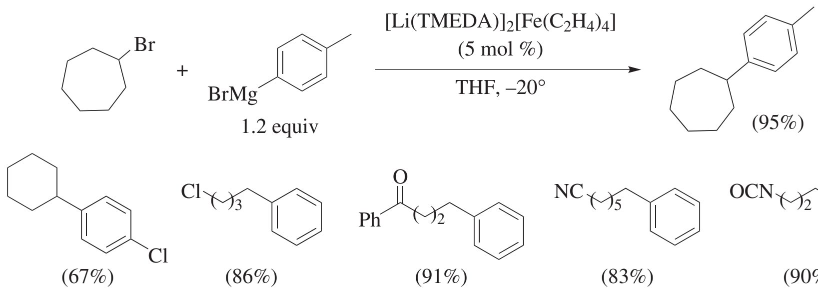


(Eq. 84)



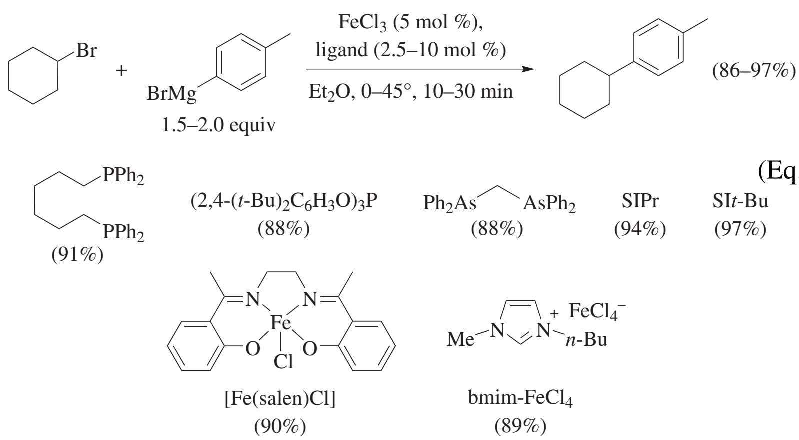
(Eq. 85)

A low-valent iron(−2)−TMEDA complex also serves as the catalyst for cross-coupling of primary and secondary alkyl halides with various arylmagnesium reagents.[114,41] Chemoselective cross-couplings are feasible in the presence of potentially reactive functional groups such as carbonyl, cyano, and isocyanato groups. A variety of primary and secondary alkyl bromides and iodides show excellent reactivities, whereas alkyl chlorides are inert under these reaction conditions (Eq. 86).[114,41]



(Eq. 86)

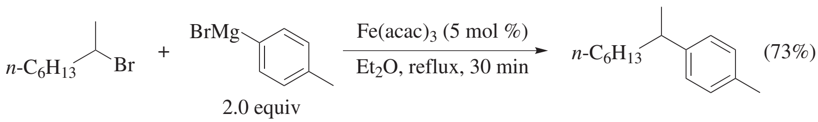
In addition to the amine ligands mentioned above, many types of ligands, including phosphines, phosphites, arsines, NHC's,[46] and salens[132] can promote iron-catalyzed cross-coupling between alkyl halides and arylmagnesium reagents (Eq. 87). These ligands show a beneficial effect on selectivity and yield. An imidazolium-derived ionic liquid possessing a ferrate counteranion, which could be a good precursor for the generation of iron−carbene species, serves as a catalyst for cross-coupling (Eq. 87).[133] Notably, the catalyst is recyclable and the reaction can be performed without losing significant activity over five cycles.



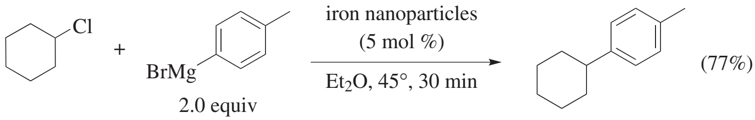
(Eq. 87)

The iron-catalyzed cross-coupling of alkyl chlorides, bromides, and iodides with arylmagnesium reagents takes place even in the absence of amine ligands: $Fe(acac)_3$ in diethyl ether is reported to give cross-coupling products, although the

yield obtained is moderate (Eq. 88).[49] "Iron nanoparticles," formed by the reduction of $FeCl_3$ with organomagnesium compounds in the presence of polyethylene glycol (PEG 14000), can catalyze the cross-coupling of cyclohexyl chloride with 4-tolylmagnesium bromide without an additive to give the product in 77% yield (Eq. 89).[134]

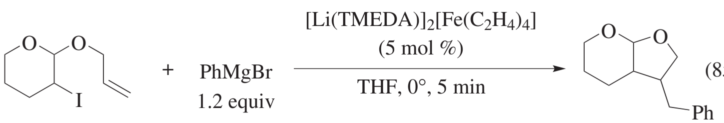


(Eq. 88)



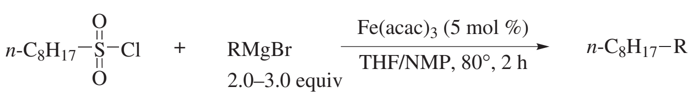
(Eq. 89)

Iron-catalyzed tandem cyclization/cross-coupling can be achieved with alkyl halides possessing an appropriately placed internal alkene. The substrates undergo ring closure prior to the cross-coupling, presumably through an alkyl radical intermediate. The reaction provides a useful method for the preparation of novel carbocycles and heterocycles (Eq. 90[114]).[66,131,46,134,41]



(Eq. 90)

In the presence of $Fe(acac)_3$, a variety of sulfonyl chlorides, including primary and secondary alkyl, alkenyl, and aryl sulfonyl chlorides, undergo desulfinylative cross-coupling with aryl- and alkenylmagnesium reagents (Eq. 91).[61] However, the reaction with allyl- and benzylmagnesium reagents gives only decomposition products.

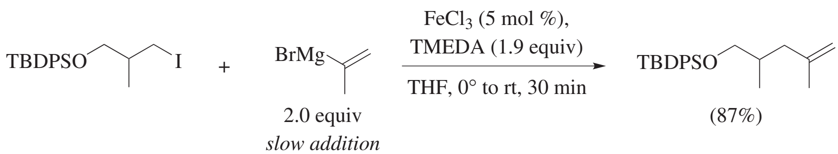


R	
R = Ph	(72%)
CH_2=C(Me)	(46%)
$PhCH_2CH_2$	(6%)
CH_2=$CHCH_2$	(0%)

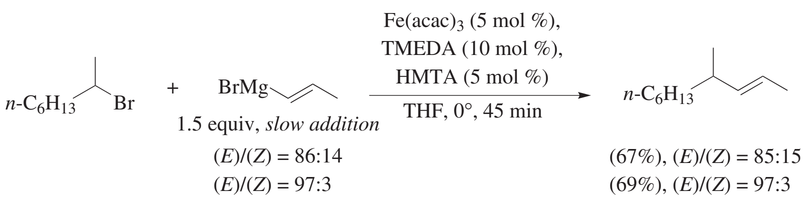
(Eq. 91)

Alkenylmagnesium reagents can be employed for iron-catalyzed cross-coupling of alkyl electrophiles. A catalytic amount of $FeCl_3$ and a stoichiometric amount of TMEDA is reported to be a suitable catalyst combination for the efficient cross-coupling reaction of unactivated alkyl halides with alkenylmagnesium reagents (Eq. 92).[47] The catalytic system consisting of

$Fe(acac)_3$, TMEDA, and HMTA is also effective (Eq. 93).[55] Under both sets of conditions, a variety of primary and secondary alkyl halides react stereospecifically (at the sp^2 carbon) with alkenylmagnesium reagents to afford coupling products in good to excellent yields.

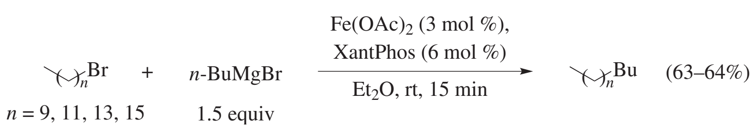


(Eq. 92)



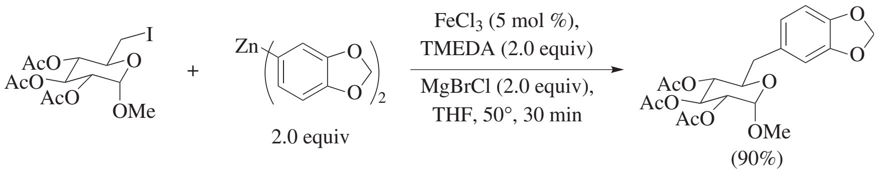
(Eq. 93)

In general, transition-metal-catalyzed $C(sp^3)-C(sp^3)$ cross-coupling is particularly challenging. The combination of $Fe(OAc)_2$ and XantPhos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) catalyzes $C(sp^3)-C(sp^3)$ cross-coupling between primary or secondary alkyl halides and primary alkylmagnesium reagents, although the yields obtained are rather low. The cross-coupling reaction of 1-bromodecane and its congeners with *n*-butylmagnesium bromide affords the products in 63% to 64% yield (Eq. 94).[135]

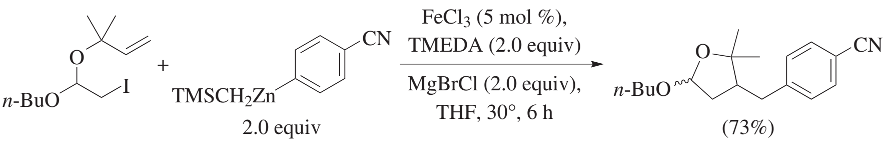


(Eq. 94)

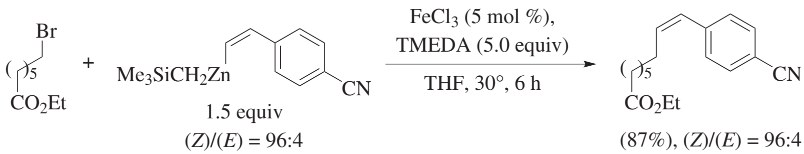
Reactions with Organozinc Compounds. Organozinc compounds participate in iron-catalyzed cross-coupling reactions with alkyl halides and sulfonates in the presence of a stoichiometric amount of TMEDA.[136,137,56] The use of organozinc compounds, which are less nucleophilic than organomagnesium compounds, allows highly chemoselective cross-couplings between functionalized alkyl halides and organozinc compounds (Eq. 95).[136] It should be noted that the presence of Lewis acidic salts such as $MgBr_2$ is critical to achieve an effective catalytic transformation. Tandem cyclization/cross-coupling is also possible under these reaction conditions (Eq. 96).[136] When alkenylzinc reagents are used, the addition of an excess amount of TMEDA is crucial to obtain a high yield of cross-coupling products (Eq. 97).[56]



(Eq. 95)

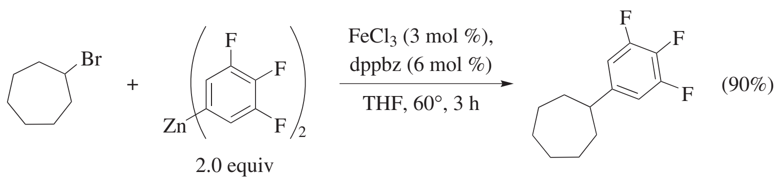


(Eq. 96)



(Eq. 97)

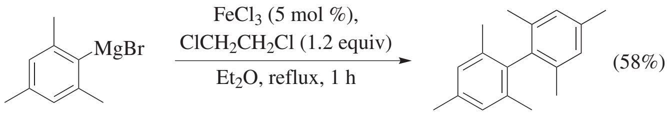
The ligand dppbz is especially useful for selective cross-coupling between alkyl halides and perfluorinated arylzinc compounds (Eq. 98),[138] which is unachievable using other additives such as TMEDA. This cross-coupling protocol provides easy and practical access to the synthesis of perfluorinated aromatic compounds.



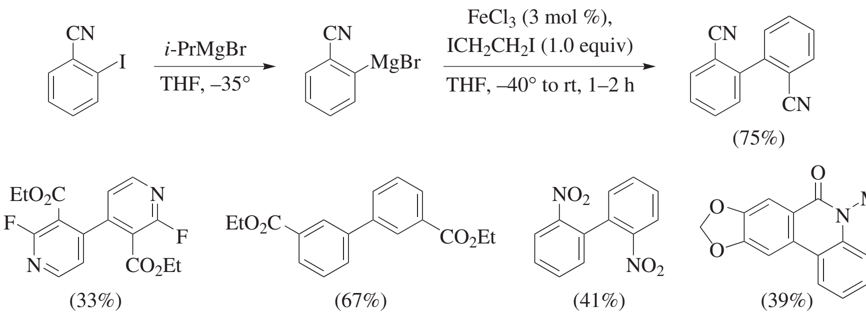
(Eq. 98)

Oxidative and Reductive Coupling Reactions

Oxidative Coupling Reactions. Iron catalysts function effectively in oxidative homocoupling reactions of arylmagnesium reagents. A variety of aryl- and heteroarylmagnesium reagents undergo iron-catalyzed homocoupling to give symmetrical biaryls in the presence of a 1,2-dihaloethane as a stoichiometric oxidant.[139,140] Bulky arylmagnesium reagents including a reagent possessing two *ortho*-substituents can participate in the reaction, although the yield is moderate (Eq. 99).[139] The homocoupling reaction is highly chemoselective, as shown by the fact that a range of reactive functional groups such as cyano, carbonyl, and nitro groups are tolerated. Various functionalized arylmagnesium reagents prepared from a halogen–magnesium exchange reaction undergo the homocoupling reaction in low to moderate yields (Eq. 100).[140] Intramolecular coupling reactions to construct a fused ring system have also been reported.[140]

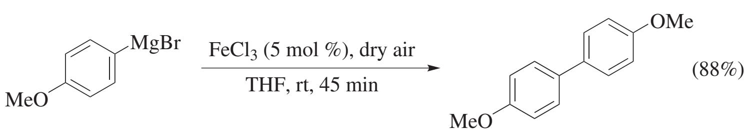


(Eq. 99)

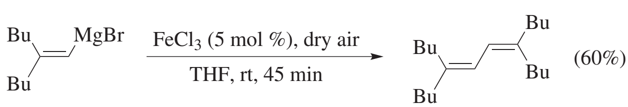


(Eq. 100)

Oxygen can be used instead of an organic oxidant. Thus, dry air is successfully employed for oxidative homocoupling reactions of aryl- and alkenylmagnesium reagents to afford various biaryl or diene compounds in good yields (Eqs. 101 and 102).[57] A manganese salt, $MnCl_2$•2LiCl, also efficiently catalyzes the oxidative homocoupling reaction of organomagnesium reagents using atmospheric oxygen as the oxidant.[57]

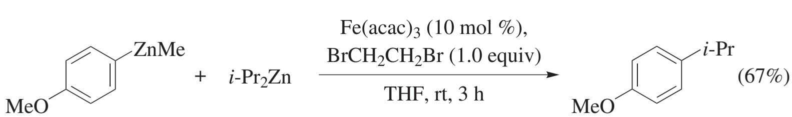


(Eq. 101)



(Eq. 102)

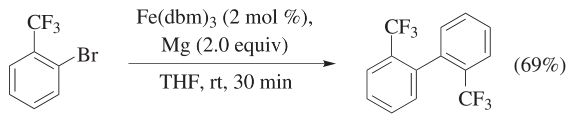
Iron-catalyzed oxidative cross-coupling between sp^2- and sp^3-carbon nucleophiles can be achieved using organozinc compounds. A variety of aryl(methyl) zinc compounds can couple with dialkylzincs in the presence of $Fe(acac)_3$ and 1,2-dibromoethane as the oxidant to give the alkylated arenes in moderate to good yields (Eq. 103).[141] Primary and secondary alkylzinc compounds react well as the sp^3-carbon nucleophilic partners, whereas tertiary alkyl-, allyl-, and benzylzinc compounds are not usable.



(Eq. 103)

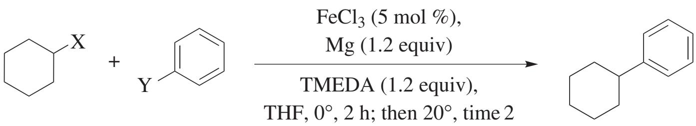
Reductive Coupling Reactions. The reductive homocoupling reaction of alkyl halides in the presence of a stoichiometric amount of a reducing agent such

as sodium or magnesium is known as Wurtz-type coupling. Some iron salts, such as $Fe(dbm)_3$, efficiently catalyze Wurtz-type coupling of primary and secondary alkyl and benzyl bromides using magnesium as a stoichiometric reductant.[142] The iron catalysis can be applied to reductive homocoupling reactions of aryl bromides (Ullmann-type coupling)[143,144] to give symmetrical biaryl compounds.[142] Primary and secondary alkyl, and benzyl bromides can be coupled to give the products in low to moderate yields. Notably, strong electron-withdrawing groups such as trifluoromethyl are tolerated under the reaction conditions (Eq. 104).[142]



(Eq. 104)

Reductive cross-coupling reactions between aryl halides and alkyl halides are catalyzed by $FeCl_3$/TMEDA in the presence of magnesium as the stoichiometric reductant (Eq. 105).[145] This one-pot protocol has the merit that it avoids the preparation and manipulation of aryl or alkyl Grignard reagents. The use of aryl or alkyl chlorides is also possible, but the yields of the cross-coupling products are considerably decreased.



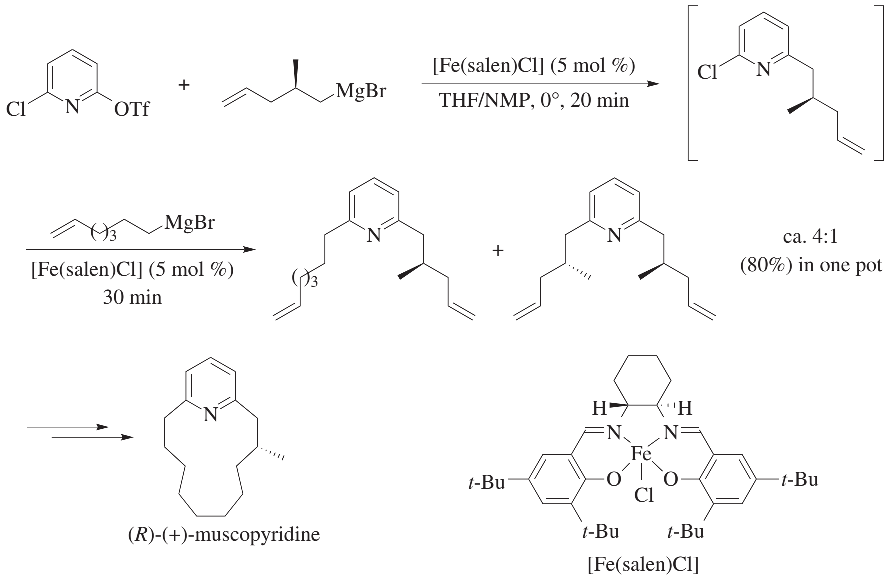
X	Y	Time 2 (h)	Yield (%)
Br	Br	2	77
Cl	Br	2	25
Br	Cl	3	20

(Eq. 105)

APPLICATIONS TO SYNTHESIS

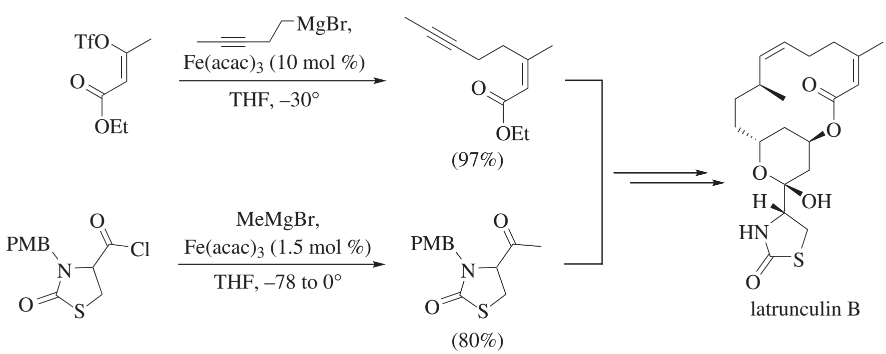
Iron is a promising cross-coupling catalyst because of its practical advantages over palladium and other transition metals, as well as its unique catalytic activity. In recent years, several natural product syntheses have been accomplished using iron-catalyzed cross-coupling reactions between alkylmagnesium reagents and sp^2-carbon electrophiles. For instance, an efficient total synthesis of the odoriferous alkaloid (*R*)-(+)-muscopyridine was accomplished in 2003 (Scheme 9).[65] The key step is the successive cross-couplings of a bifunctional pyridine derivative with an enantiomerically pure alkylmagnesium reagent and 6-heptenylmagnesium bromide in one pot. The authors take advantage of the high catalytic activity of iron under very mild reaction conditions to achieve selective $C(sp^2)-OTf$ bond cleavage in the presence of a $C(sp^2)-Cl$ bond[146] and without racemization of the optically active reagent. Although the selectivity is not complete, the undesired minor byproduct is removed by "chemical self-clearance," wherein after selective ring-closing metathesis of the major product,

the remaining byproduct is polymerized and easily removed. This key step allows an expeditious total synthesis of (*R*)-(+)-muscopyridine with good overall yield and step economy.



Scheme 9. Synthesis of (*R*)-(+)-muscopyridine.

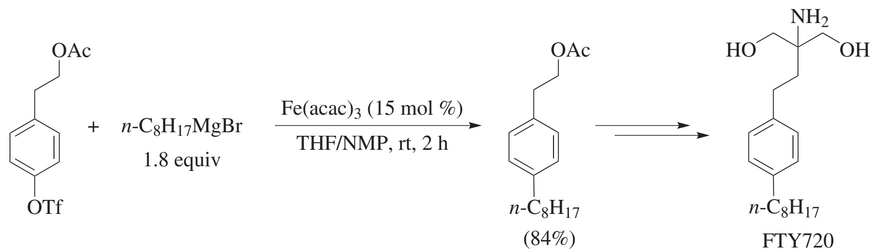
A concise and productive route to latrunculin B, isolated as the ichthyotoxic component of the Red Sea sponge *Latrunculia magnifica*,[147] has been developed based on iron-catalyzed cross-coupling. Two key intermediates are prepared from an alkenyl triflate and 3-pentyn-1-ylmagnesium bromide, and from an acyl chloride and methylmagnesium bromide, respectively (Scheme 10).[148] The iron-catalyzed cross-coupling of an alkyne-containing alkylmagnesium reagent with an enol triflate possessing an ester group proceeds under mild conditions in quantitative yield and with good tolerance for the ester group. Methylation of the acyl



Scheme 10. Synthesis of latrunculin B.

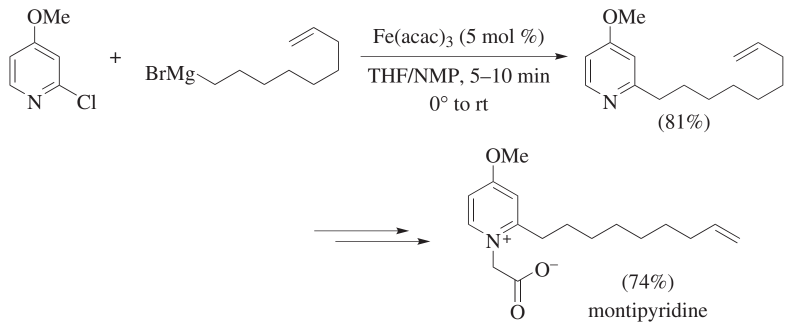
chloride with methylmagnesium bromide can proceed in the absence of a catalyst, but the iron-catalyzed reaction is faster and more reliable. Notably, the reaction using dimethylcuprate as the methyl donor results in complete decomposition of the starting material.

The high chemoselectivity of iron-catalyzed cross-couplings is exploited in the total synthesis of the potent immunosuppressive agent FTY720 (Scheme 11).[149] In the presence of $Fe(acac)_3$ and NMP as a cosolvent, the reaction of an aryl triflate possessing an ester group with octylmagnesium bromide takes place smoothly to give the cross-coupling product. Addition of the alkylmagnesium reagent to the ester group is not observed.



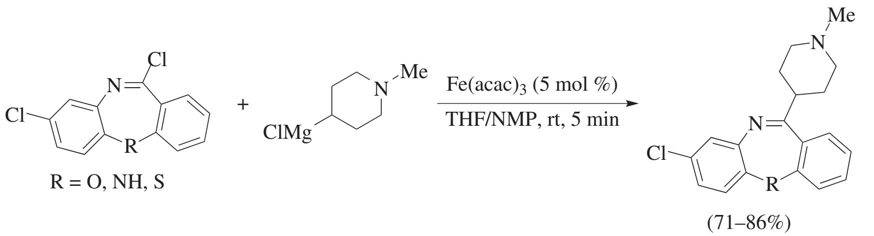
Scheme 11. Synthesis of FTY720.

A key intermediate in the synthesis of montipyridine, a cytotoxic marine natural product isolated from the stony coral *Montipora sp*,[150] is prepared by iron-catalyzed cross-coupling of a chloropyridine derivative with 8-nonenylmagnesium bromide (Scheme 12).[85] This reaction proceeds rapidly at room temperature without the need of a ligand.



Scheme 12. Synthesis of montipyridine.

Analogues of the antipsychotic agent clozapine can be prepared in good yield by the reaction of imidoyl chlorides with alkylmagnesium reagents in the presence of an iron catalyst and an excess amount of NMP (Eq. 106).[146] The aryl chloride group is not affected under these mild conditions. The reaction in the absence of the iron catalyst proceeds much slower and in low yield.



(Eq. 106)

Recently, the substrate scope of iron-catalyzed cross-coupling has been extended by using functionalized organomagnesium and organozinc reagents.[151] These advances will provide further opportunities in the synthesis of highly functionalized molecules, such as pharmaceuticals, pesticides, liquid crystals, optoelectronic materials, etc.

COMPARISON WITH OTHER METHODS

Thorough comparison between iron-catalyzed cross-coupling reactions and the enormous literature on palladium- or other transition-metal-catalyzed cross-couplings[152] is impractical here. However, this section briefly touches on several selected aspects of comparison of the methods.

The major advantages of iron catalysts over other transition metals are their abundance, low cost, and nontoxicity. Another important characteristic of iron catalysis is the high activity of a suitably designed catalyst, which allows one to accomplish a fast reaction under mild reaction conditions. Therefore, in many reactions, iron-catalyzed cross-couplings show good functional-group tolerance, sometimes surpassing that found with palladium or nickel catalysis.[114] It should be noted though that, besides the catalyst, the choice of the reagents is also important. For example, palladium catalysis allows one to achieve efficient reactions with less reactive boron or tin compounds, whereas iron catalysis has been exploited much less with these reagents, but rather has been applied with the more reactive organomagnesium and organozinc reagents.

The high activity of iron catalysts may present disadvantages, such as difficulties in controlling the reaction pathway and faster catalyst deactivation, requiring rather high catalyst loadings. These issues have been solved for palladium catalysis by the development of a plethora of efficient stabilizing ligands,[152] which allow highly selective reactions and extremely low catalyst loadings, reaching ppm and ppb levels. Although efficient ligands and additives have been developed for iron, truly high-efficiency ligands comparable to those used in palladium chemistry are still lacking.

Regarding the electrophilic partner, iron catalysts can achieve chemoselectivity that is complementary to other transition metals, such as palladium and nickel. Whereas palladium and nickel catalysts react the fastest with aryl iodides and bromides, iron catalysts can prefer chlorides, triflates, or tosylates. For example,

the iron-catalyzed reactions of an alkylmagnesium bromide with aryl chlorides, triflates, and tosylates lead to almost quantitative formation of the desired cross-coupling product, whereas the corresponding aryl bromides and iodides react in low yields[85] because the high reactivity of iron toward these electrophilic partners leads to poor chemoselectivity. In contrast, in the presence of a nickel or palladium catalyst, aryl bromides and iodides give the coupling products in good yields.[90,91] The iron-catalyzed cross-coupling of arylzinc compounds with benzyl halides and phosphates tolerates a bromine substituent on the aromatic ring of benzylic electrophiles,[129] whereas this selectivity cannot be achieved using nickel or palladium catalysis.[130]

Although a variety of transition metals including nickel, palladium, cobalt, and copper efficiently catalyze the cross-coupling reactions of unactivated alkyl electrophiles with arylmetal reagents,[130,20] the reactivity and selectivity of iron catalysis toward unactivated alkyl halides is remarkable. Vanadium[153] and silver[154,155] catalysts are also reported to promote the $C(sp^3)-C(sp^2)$ cross-coupling reaction, but the yield and selectivity still need to be improved. In contrast, iron-catalyzed cross-coupling reactions with organomagnesium, -zinc, -aluminum, and -boron compounds show broader applicability for a variety of nonactivated alkyl halides, including secondary alkyl chlorides.

Organic iodides, bromides, and chlorides can be used in iron-catalyzed cross-coupling reactions, but iron-catalyzed reactions of organic fluorides have not been reported to date. In contrast, other transition metals, especially nickel, are known to catalyze carbon–fluorine bond activation of aromatic fluorides.[156–158]

Regarding the organometallic reagent to be employed for the coupling reaction, palladium and nickel catalysts are extremely versatile, allowing organomagnesium, -zinc, -boron, -tin, and -silicon reagents among others to effectively take part in the reaction.[152] In contrast, iron catalysis engages a much narrower repertoire of organometallic reagents. Organomagnesium and organozinc reagents have been used extensively, but the less reactive boron, tin, and silicon have rarely been used for iron catalysis[98,99] despite their advantages, such as selectivity, stability, and ease of handling.

The palladium- and other transition-metal-catalyzed reaction of an organic halide with an alkene (the Heck reaction) is a versatile method to construct stereodefined polysubstituted alkenes.[159,160] Iron catalysis is lagging behind in this field, and only one example of an iron-catalyzed Heck reaction has been reported to date;[161] only styrenes can be utilized as the alkene partner and the yields are modest.

Transition-metal-catalyzed $C(sp^3)-C(sp^3)$ cross-coupling is particularly challenging, and can be achieved through the cross-coupling of an unactivated alkyl halide with an alkylmagnesium reagent catalyzed by manganese,[162] copper,[163–167] cobalt,[168–171] nickel,[172–175] and palladium.[176,177,173] The $C(sp^3)-C(sp^3)$ cross-coupling between an alkyl halide and an alkylmagnesium reagent using iron catalysis has been reported once, but the yields are low and the scope is rather narrow.[135]

Enantioselective cross-couplings have been achieved using palladium[177a] or nickel catalysis,[178,179] but there are no such reports to date using iron catalysis, which remains a future challenge for the development of iron-catalyzed cross-couplings.

EXPERIMENTAL CONDITIONS

Many experimental variables are critical to the success of iron-catalyzed cross-coupling reactions. The following section provides an overview of iron sources, additives, ligands, organometallic compounds, and other conditions that can provide guidelines for the initial selection of reaction conditions.

The Iron Source

Among the commercially available iron(+2) and iron(+3) sources, $Fe(acac)_3$ is the most versatile and common catalyst precursor because of its catalytic performance, low cost, and stability. More expensive analogues of $Fe(acac)_3$, $Fe(dbm)_3$ and $Fe(dpm)_3$, can also be employed. Iron(+3) chloride shows comparable (or higher in some cases) catalytic performance and can be the second-choice catalyst precursor, although careful handling is required due to its hygroscopic nature. Iron(+2) sources, particularly $FeCl_2$, can be a third choice, having a potential advantage in reducing side reactions such as homocoupling of organometallic reagents accompanying an initial reduction process. However, there is a trade-off between this advantage and the lack of solubility in ethereal solvents, and thus catalyst screening is often required on a case-by-case basis. Less soluble iron(+2 or +3) sources such as iron oxides, iron hydroxides, and iron fluorides are generally inefficient catalyst precursors owing to strong coordination of the counteranions. As a consequence, one of the three iron sources ($Fe(acac)_3$, $FeCl_3$, and $FeCl_2$) gives the optimum yield in almost all reactions with the following exceptions: $FeF_3{\bullet}3H_2O$ gives high selectivity for cross-coupling over homocoupling in the reaction of aryl halides with arylmagnesium reagents, whereas other iron sources give poor selectivity.[93,94] The reaction of alkyl halides with alkylmagnesium reagents takes place in moderate yields with $Fe(OAc)_2$, but in poor yields with other iron sources.[135] Fluoride and acetate ions are assumed to remain coordinated to the iron center during the reactions. A new class of iron complexes, $[Li(TMEDA)]_2[Fe(C_2H_4)_4]$ and $FeCl_2(dppbz)_2$,[99,129,138] shows higher catalytic performance than the conventional iron sources in the reactions of alkyl halides with arylmagnesium,[114,41] -zinc,[129,138] and -boron[99] compounds. Iron(0) carbonyl $[Fe_2(CO)_9]$ and its complexes, such as $Bu_4N[Fe(CO)_3NO]$ and $Na[Fe(CO)_3NO]$, are essential catalysts for allylation of active methylene compounds.[115–117,119–122]

Additives and Ligands

Most of the early investigations from the 1970's to the 1990's did not employ particular additives. In more recent reports,[62,63,179a,84] many iron-catalyzed cross-coupling reactions of sp^2-carbon electrophiles with alkyl- and arylmagnesium reagents have benefited from the addition of excess amounts of NMP.[54,180,69,60,73,146,85,43,65,87,61,149,180a,72,88,89,41] NMP is best purified by

distillation just before use.[181] Lithium chloride and lithium bromide are also effective additives for the coupling reactions of sp^2-carbon electrophiles.[58,68] Lithium salts can be purified by recrystallization from water, methanol, or ethanol, and dried in vacuo at 100–130°.[181] A difficult class of coupling partners, sp^3-carbon electrophiles, efficiently couple with aryl(alkenyl)magnesium and -zinc compounds using a stoichiometric amount of TMEDA as the additive.[66,131,47,136,137,56,145] The combined use of a catalytic amount of TMEDA and HMTA is comparable to a stoichiometric amount of TMEDA.[48,55] TMEDA and HMTA can be purified by distillation from BuLi and recrystallization from absolute ethanol, respectively.[181] In contrast to palladium- and nickel-catalyzed cross-coupling reactions, there are only a few iron-based reactions mediated by phosphorus ligands, such as the Tsuji–Trost reaction by Ph_3P,[120] the reaction of alkyl halides with alkylmagnesium reagents by XantPhos,[135] and the reaction of alkyl halides with arylzinc[129,138] and -boron[99] compounds by dppbz. The bulky NHC ligands SIPr and SIMes show good catalytic activity for the reaction of aryl halides with arylmagnesium reagents[93,94] and the reaction of alkenyl carboxylates with alkylmagnesium reagents,[68] respectively. The phosphine ligands and carbene precursors mentioned above can be purchased from commercial suppliers and used as received.

Organometallic Compounds

Organomagnesium compounds (Grignard reagents) are readily prepared from the corresponding organic halides or are available from commercial suppliers, and are often the first choice in iron-catalyzed cross-coupling reactions. However, the cross-coupling reactions with organomagnesium compounds have a limitation of functional-group compatibility because of their highly nucleophilic and basic properties. Halogen–magnesium exchange between an aryl halide and a 2-propylmagnesium halide at low temperature provides a partial remedy: a variety of arylmagnesium compounds possessing ester, cyano, and nitro groups were prepared from the corresponding aryl halides in situ and coupled with alkenyl halides[70] and aroyl cyanides[83] at low temperatures. Treatment of the functionalized arylmagnesium compounds with copper cyanide affords the corresponding arylcopper compounds of considerable thermal stability. These reagents can be employed in coupling reactions even at 80°, at which temperature some functional groups remain intact.[77,96,97] Organozinc compounds are a useful class of organometallic compounds because of their ready availability and functional-group compatibility. A variety of aryl and alkenylzinc compounds have been employed in the coupling reactions of alkyl halides[136–138,56] or acyl chlorides,[84] and can be a second choice. Organomanganese compounds are also useful coupling partners.[62,63,179a] Although organoboron compounds are the most versatile organometallic compounds because of their stability, high functional-group compatibility, and commercial availability, there are only two reports of iron-catalyzed cross-coupling employing organoboron compounds. One example is the reaction of aryl bromides with phenylboronic acid at 15000 bar,[98] and the other is the reaction of benzyl halides with tetraarylborates.[99]

Other Conditions

The cross-coupling reactions must be carried out under an inert gas atmosphere to suppress deactivation of the iron catalysts or unfavorable side reactions, such as homocoupling reactions induced by molecular oxygen.[57] Most of the coupling reactions take place smoothly in ethereal solvents (Et_2O, THF, DME, MTBE, 1,4-dioxane) or toluene with or without additives under low to ambient temperature. The Tsuji–Trost-type reactions[115–117,119–122] and the Sonogashira reaction[64,108,109] require elevated temperatures and/or aprotic polar solvents (DMF, $MeNO_2$). The order of adding the reagents can significantly increase the yield in many cases. In general, the organometallic compound is added to a mixture of the electrophile and the catalyst precursor to avoid over-reduction or probable ferrate formation from the iron precursor. In particular, in the reactions between sp^3-carbon electrophiles and Grignard reagents, the slow addition of Grignard reagents significantly improves the product yield.[66,114,48,55,47,61,41] The most common workup procedures involve quenching the reaction with acid, such as aqueous HCl or NH_4Cl, followed by extraction with an organic solvent. Purification by distillation or silica gel column chromatography affords analytically pure products.

EXPERIMENTAL PROCEDURES

The experimental procedures provided in this section exemplify the reaction protocols described in the text. Many are derived from general procedures described in the primary literature, and, where necessary, weights and volumes of reagents based on equivalency have been added for specific substrates and reagents as an aid to the reader. Before preparing any of the compounds included in this section, the reader should consult the original reference.

Iron(+3) Chloride, $FeCl_3$.[182] Iron(+3) chloride was purchased from a commercial supplier, dehydrated with $SOCl_2$ and dried thoroughly under reduced pressure to give anhydrous $FeCl_3$.

tris(Acetylacetonato)iron(+3), $Fe(acac)_3$.[183] Anhydrous $FeCl_3$ (4.0 g, 24.7 mmol) was dissolved in water (6 mL) with gentle warming. Ammonia solution (9 mL) was added slowly with constant stirring. The mixture was heated on a steam bath for 15–20 min, and the precipitate of iron(+3) hydroxide was then collected by filtration and washed with water until free from chloride. The moist iron(+3) hydroxide and acetylacetone (12.0 g, 120 mmol) were placed in a small conical flask, the neck of which was plugged with cotton wool, and the whole was heated on a steam bath for 35 min. On cooling, large red crystals were obtained, which were dried on filter paper and recrystallized from EtOH to give $Fe(acac)_3$ (7.85 g, 90%): mp 175°.

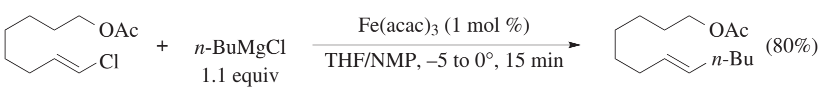
tris(Dibenzoylmethido)iron(+3), $Fe(dbm)_3$.[28] A 200-mL, two-necked, round-bottomed flask containing $FeCl_3{\bullet}6H_2O$ (1.2 g, 4.4 mmol), water (10 mL), and a magnetic stir bar was fitted with a rubber septum and a three-way

stopcock connected to a balloon filled with nitrogen. The mixture was stirred with external heating until homogeneous. A solution of 1,3-diphenylpropane-1,3-dione (3.7 g, 17 mmol) in EtOH (35 mL) was added. The mixture was heated until homogeneous. Ammonia solution (25%) was added dropwise to adjust the mixture to pH 8. After 3 h, the resultant red precipitate was collected by filtration, and the precipitate was dried under reduced pressure. After recrystallization from benzene/hexane, $Fe(dbm)_3$ was obtained as purple needles (2.7 g, 85%): mp 240° (dec).[52]

Chlorido[(*R*,*R*)-(−)-*N*,*N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]iron, Fe(salen)Cl.[43] A solution of (*R*,*R*)-(−)-*N*,*N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (1.0 g, 1.8 mmol) in THF (5 mL) was added to a suspension of NaH (86 mg, 3.6 mmol) in THF (5 mL) at 0°. After the evolution of gas ceased, the mixture was heated at reflux for 2 h and cooled to rt before $FeCl_3$ (0.43 g, 2.6 mmol) was introduced and reflux was continued for 4 h. Standard extractive workup followed by evaporation of the solvent provided the title complex as a dark-red solid (1.0 g, 87%; reported in reference as 95%): IR (film) 2955, 2906, 2866, 1610, 1553, 1536, 1462, 1433, 1389, 1361, 1345, 1311, 1253, 1174 cm^{-1}; MS m/z (% relative intensity): M^+ 635 (100), 620 (25), 600 (15), 584 (43), 569 (16), 277 (20).

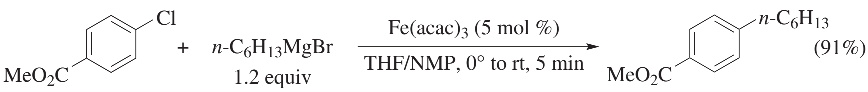
tris(*N*,*N*,*N′*,*N′*-Tetramethylethylenediamine)bis(trichloridoiron), $(FeCl_3)_2(TMEDA)_3$.[48] A dry 250-mL flask, equipped with a mechanical stirrer and a septum, was charged with $FeCl_3$ (3.24 g, 20.0 mmol) in THF (200 mL). After complete dissolution of the $FeCl_3$, anhydrous *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (3.48 g, 30.0 mmol) was slowly added via a syringe. A light brown powder precipitated immediately. The complex, $(FeCl_3)_2(TMEDA)_3$, was isolated by filtration and washing with THF (50 mL) (3.27 g, 49%; reported in reference as 97%).

Dichlorido(*N*,*N*,*N′*,*N′*-tetramethylethylenediamine)zinc, $ZnCl_2$ (TMEDA).[184] The complex was prepared by mixing a saturated solution of $ZnCl_2$ in THF (19 mL) and TMEDA (5 mL) and allowing the solution to stand for several hours at rt. The crude crystals that separated were collected and recrystallized from THF to obtain $ZnCl_2$(TMEDA) in nearly quantitative yield.

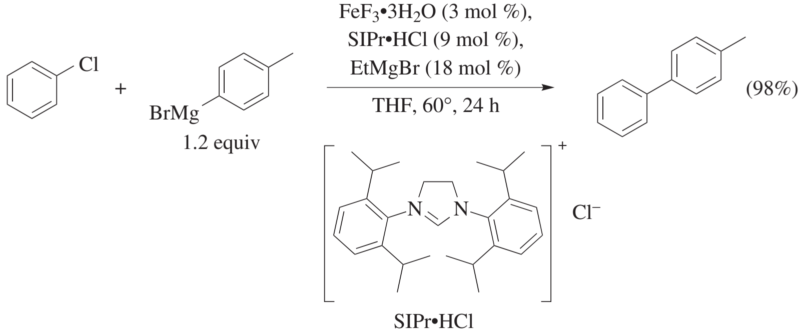


12-Acetoxydodec-5-ene [Cross-Coupling of an Alkenyl Chloride with an Alkylmagnesium Compound in the Presence of NMP].[54] *n*-Butylmagnesium chloride (1.2 M solution in THF, 22.9 mL, 27.5 mmol) was added dropwise over 10 min, between −5 and 0°, to a solution of (*E*)-8-acetoxy-1-chlorooct-1-ene (5.11 g, 25.0 mmol) and $Fe(acac)_3$ (0.088 g, 0.25 mmol) in a mixture of THF

(30 mL) and NMP (25 mL). After stirring was continued for 15 min, the reaction mixture was hydrolyzed at -10° with aqueous HCl solution (1 M, 80 mL). After decanting, the aqueous layer was extracted with Et_2O and the combined organic phases were washed with saturated, aqueous $NaHCO_3$ solution, water, and dried with $MgSO_4$. The solvents were removed in vacuo and the product was isolated by distillation (4.53 g, 80%): bp 120–123°/5 mm Hg; IR (neat) 1742, 968, 724 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, $J = 5.6$ Hz, 3H), 1.25–1.50 (m, 8H), 1.66–1.68 (m, 2H), 2.03–2.11 (m, 6H), 2.11 (s, 3H), 4.10–4.15 (m, 2H), 5.43–5.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5, 20.4, 21.8, 25.4, 28.3, 28.4, 29.1, 31.5, 31.9, 32.1, 64.1, 129.7, 130.1, 137.1.

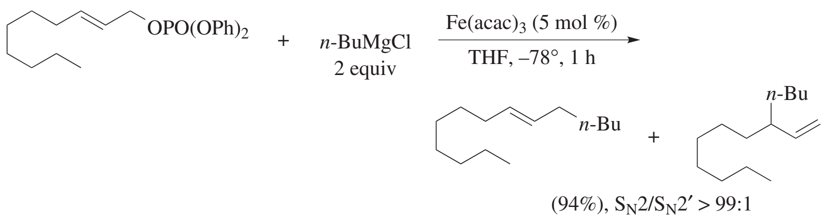


Methyl 4-Hexylbenzoate [Cross-Coupling of an Aryl Chloride with an Alkylmagnesium Compound in the Presence of NMP].[43] A flame-dried, two-necked flask was charged under argon with methyl 4-chlorobenzoate (1.00 g, 5.86 mmol), $Fe(acac)_3$ (103 mg, 0.292 mmol), THF (35 mL), and NMP (3.3 mL). A solution of hexylmagnesium bromide (2.0 M in Et_2O, 3.5 mL, 7.0 mmol) was added to the resulting red solution using a syringe, causing an immediate color change to dark brown and then finally to violet. The resulting mixture was stirred for 5–10 min, then was diluted with Et_2O, and was carefully quenched by the addition of an aqueous HCl solution (1 M, 10 mL). Standard extraction followed by silica gel chromatography of the crude product (hexane/EtOAc 30:1) provided methyl 4-hexylbenzoate as a colorless syrup (1.24 g, 96%; reported in reference as 91%): IR 1724 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, $J = 6.9$ Hz, 3H), 1.21–1.29 (m, 6H), 1.57 (m, 2H), 2.59 (t, $J = 7.7$ Hz, 2H), 3.84 (s, 3H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.90 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 28.9, 31.0, 31.2, 35.9, 51.8, 127.6, 128.7, 129.2, 148.4, 167.1; EIMS m/z (% relative intensity): M$^+$ 220 (50), 189 (39), 150 (100), 91 (54), 43 (17).

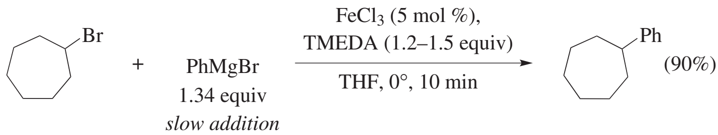


4-Methylbiphenyl [Cross-Coupling of an Aryl Chloride with an Arylmagnesium Compound in the Presence of an NHC Ligand].[93] Iron(+3) fluoride

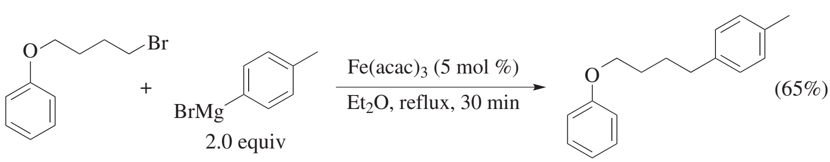
trihydrate (0.150 g, 0.899 mmol) and 1,3-bis(2,6-diisopropylphenyl)imidazolium hydrochloride (1.15 g, 2.70 mmol) were added to a solution of ethylmagnesium bromide (1.08 M in THF, 5.00 mL, 5.40 mmol) at 0°. Tetrahydrofuran (1.0 mL) was added to rinse the vessel. After the reaction mixture was stirred at rt for 5 h, chlorobenzene (3.38 g, 30.0 mmol) and 4-methylphenylmagnesium bromide (1.02 M solution in THF, 35.3 mL (reported in reference as 38.7 mL), 36.0 mmol) were added at 0°. The reaction mixture was stirred at 60° for 24 h. After the reaction mixture was cooled to rt, aqueous sodium potassium tartrate (saturated, 60.0 mL) was added. The aqueous layer was extracted five times with hexane. The combined organic extracts were filtered through a pad of Florisil. After the solvent was removed in vacuo, the crude product was purified by chromatography on silica gel (pentane) to obtain 4-methylbiphenyl (4.97 g, 98%, >98% pure on GC analysis) as a white solid: mp 49–50°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 7.15 (d, J = 7.9 Hz, 2H), 7.22 (m, 1H), 7.32 (t, J = 8.2 Hz, 2H), 7.40 (d, J = 7.4 Hz, 2H), 7.49 (m, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 126.9 (3C), 127.1 (2C), 128.7 (2C), 129.4 (2C), 137.0, 138.3, 141.1; IR (neat) 3081, 3062, 3030, 2925, 1556, 1531 cm^{-1}; LRMS (EI) m/z (% relative intensity): M$^+$ 168 (98), 152 (38), 115 (15), 91 (18), 51 (10); HRMS (EI) exact mass calcd for $C_{13}H_{12}$, 168.0939; found, 168.0926.[184a]



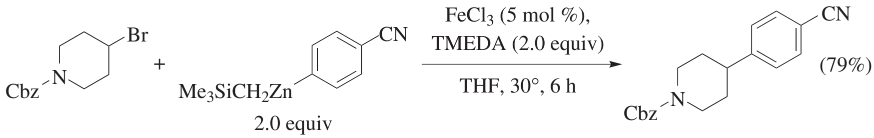
(6*E*)-Tetradec-6-ene [Cross-Coupling of an Allylic Phosphate with an Alkylmagnesium Compound].[112] A mixture of Fe(acac)$_3$ (9.0 mg, 0.025 mmol) and (*E*)-2-decen-1-yl diphenyl phosphate (194.2 mg, 0.500 mmol) was dissolved in dry THF (4 mL) under an argon atmosphere. The solution was cooled to −78° and a solution of *n*-butylmagnesium chloride (1.0 mmol) in THF was added dropwise. After stirring for 1 h at −78°, the reaction mixture was poured into a saturated, aqueous NH_4Cl solution and was extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to afford (6*E*)-tetradec-6-ene (92.3 mg, 94%): the S_N2/S_N2' ratio was determined to be > 99:1 by GC analysis. TLC R_f 0.72 (hexane); IR (neat) 2959, 2926, 2874, 2855, 1466, 1379, 967, 723 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, J = 6.3 Hz, 6H), 1.15–1.47 (m, 16 H), 1.85–2.13 (m, 4H), 5.36–5.42 (m, 2H). Anal. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37. Found: C, 85.43; H, 14.59.



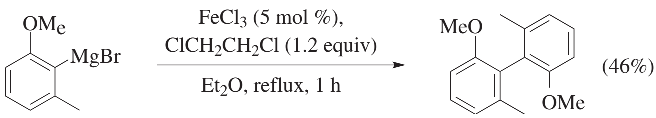
Phenylcycloheptane [Cross-Coupling of an Alkyl Bromide with an Arylmagnesium Compound in the Presence of TMEDA].[66] A mixture of phenylmagnesium bromide (0.93 M solution in THF, 72 mL, 67 mmol) and TMEDA (7.78 g, 67.0 mmol) was added at 0° via a syringe pump — at such a rate as to keep the reaction mixture a pale yellow solution (1.36 mL/min) — to a mixture of bromocycloheptane (8.85 g, 50.0 mmol) and $FeCl_3$ (0.1 M solution in THF, 25 mL, 2.5 mmol). The reaction mixture was stirred at 0° for 10 min after completion of the addition. After aqueous workup, distillation of the product mixture afforded phenylcycloheptane as a colorless oil (8.18 g containing 0.37 g of biphenyl, 90% yield): IR (neat) 3062, 3027, 2923, 2854, 1602, 1492, 1461, 1451, 1073, 1032, 753, 737, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.51–1.67 (m, 8H), 1.78–1.81 (m, 2H), 1.90–1.93 (m, 2H), 2.63–2.68 (m, 1H), 7.12–7.19 (m, 3H), 7.24–7.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.2 (2C), 27.9 (2C), 36.8 (2C), 47.1, 125.5, 126.6 (2C), 128.2 (2C), 150.0; HRMS (EI, 70 eV) m/z: M^+ calcd for $C_{13}H_{18}$, 174.1409; found, 174.1418.



4-(4-Methylphenyl)butyl Phenyl Ether [Cross-Coupling of an Alkyl Bromide with an Arylmagnesium Compound in Diethyl Ether].[49] A mixture of 4-bromobutyl phenyl ether (119 mg, 0.52 mmol) and $Fe(acac)_3$ (9.0 mg, 0.026 mmol) in Et_2O (3 mL) was warmed to reflux. 4-Methylphenylmagnesium bromide (1.67 M solution in Et_2O, 0.70 mL, 1.04 mmol) was added to this mixture, resulting in an immediate color change from red to black. The mixture was heated to reflux for 30 min, then was poured into an aqueous HCl solution (1 M), extracted with Et_2O, and the extracts were dried over $MgSO_4$. The solvent was removed and the residue was chromatographed on silica gel to give 4-(4-methylphenyl)butyl phenyl ether (81 mg, 65%): ^1H NMR ($CDCl_3$) δ 1.74–1.84 (m, 4H), 2.31 (s, 3H), 2.64 (t, J = 7.3 Hz, 2H), 3.95 (t, J = 6.0 Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 6.90–6.93 (m, 1H), 7.08 (br m, 4H), 7.24–7.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.0, 27.9, 28.9, 35.1, 67.6, 114.5, 120.5, 128.3, 129.0, 129.4, 135.2, 139.1, 159.1. Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.13; H, 8.39.

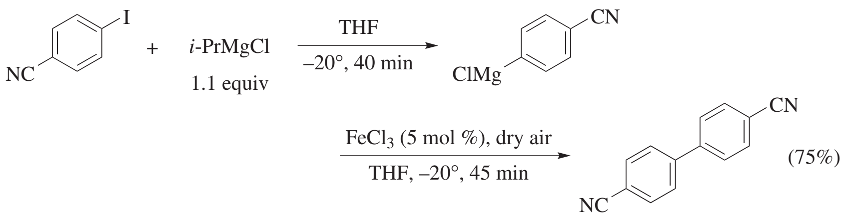


4-(4-Cyanophenyl)-*N*-(benzyloxycarbonyl)piperidine [Cross-Coupling of an Alkyl Bromide with an Arylzinc Reagent in the Presence of TMEDA].[136] In a dry reaction vessel, a mixture of 4-cyanophenylzinc bromide (0.48 M solution in THF, 4.2 mL, 2.0 mmol) and Me_3SiCH_2MgCl (1.1 M solution in Et_2O, 1.8 mL, 2.0 mmol) was stirred at 0° for 1 h. TMEDA (0.30 mL, 2.0 mmol), 4-bromo-*N*-(benzyloxycarbonyl)piperidine (298 mg, 1.00 mmol), and then $FeCl_3$ (0.1 M solution in THF, 0.5 mL, 0.05 mmol) were added to the resulting solution at 0°. The reaction mixture was stirred at 30° for 6 h. After being quenched with a saturated, aqueous solution of NH_4Cl, the mixture was filtered through a pad of Florisil and concentrated in vacuo. Purification of the residue by silica gel chromatography (hexane/EtOAc 20:1) afforded 4-(4-cyanophenyl)-*N*-(benzyloxycarbonyl)piperidine (253 mg, 79%): IR (neat) 3014, 2943, 2923, 2856, 2227, 1688 (C=O), 1466, 1455, 1436, 1273, 1218, 1125, 1057, 1009, 917, 838, 760, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58–1.70 (m, 2H), 1.78–1.90 (m, 2H), 2.74 (tt, J = 12 Hz, 3.5 Hz, 1H), 2.89 (br s, 2H), 4.35 (br s, 2H), 5.16 (br s, 2H), 7.26–7.39 (m, 7H), 7.59 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.6 (2C), 42.7, 44.3 (2C), 67.2, 110.3, 118.8, 127.6 (2C), 127.9 (2C), 128.0, 128.5 (2C), 132.4 (2C), 136.7, 150.8, 155.2. Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.80; H, 6.42; N, 8.54.



2,2′-Dimethoxy-6,6′-dimethyl-1,1′-biphenyl [Homocoupling of an Arylmagnesium Compound in the Presence of an Organic Dihalide as the Oxidant].[139] 2-Methoxy-6-methylphenylmagnesium bromide (117 mg, 0.520 mmol) was added to a refluxing solution of $FeCl_3$ (4.2 mg, 0.026 mmol) and 1,2-dichloroethane (61 mg, 0.62 mmol) in Et_2O (4 mL). After the reaction mixture was heated to reflux for 1 h, the reaction was quenched by addition of aqueous HCl solution (1 M). The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$. The volatiles were removed under reduced pressure and the residue was chromatographed on silica gel to give 2,2′-dimethoxy-6,6′-dimethyl-1,1′-biphenyl (32.3 mg, 46%) as a white solid: mp 84–85°; ^{1}H NMR ($CDCl_3$) δ 1.94 (s, 6H), 3.69 (s, 6H), 6.82 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 7.1 Hz, 2H), 7.23 (m, 2H);

^{13}C NMR ($CDCl_3$) δ 19.6, 55.8, 108.4, 122.2, 126.2, 127.9, 138.2, 157.0. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.61; H, 7.64.



4,4′-Dicyanobiphenyl [Homocoupling of an Arylmagnesium Compound Using Air as the Oxidant].[57] A dry and nitrogen-flushed 100-mL three-necked flask, equipped with a mechanical stirrer and a thermometer, was charged with 4-iodobenzonitrile (4.58 g, 20.0 mmol) and THF (10 mL). The reaction mixture was cooled to −30° and isopropylmagnesium chloride (2.0 M solution in THF, 11 mL, 22 mmol) was added dropwise. After 40 min at −20°, the I/Mg exchange was complete (checked by GC). A solution of $FeCl_3$ (0.1 M in THF, 10 mL, 1.0 mmol) was added in one portion, and dry air was immediately bubbled into the reaction mixture via a cannula. The rate of bubbling was adjusted to keep the temperature below −20°. After 45 min, the introduction of air was stopped and the reaction mixture was quenched with 1 M aqueous HCl solution (40 mL). The aqueous phase was extracted with EtOAc (3 × 20 mL) and the combined organic layers were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The product was purified by chromatography on silica gel (petroleum ether/Et_2O 97:3) to afford 4,4′-dicyanobiphenyl (1.53 g, 75%) as a white solid: mp 234°; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68–7.74 (m, 4H), 7.75–7.82 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 112.4, 118.4, 127.9, 132.8, 143.5; EIMS (70 eV) m/z (% relative intensity): 204 (100), 177 (10). Anal. Calcd for $C_{14}H_8N_2$: C, 82.33; H, 3.95; N, 13.72. Found: C, 82.55; H, 4.33; N, 13.25.

TABULAR SURVEY

The tables cover the literature through 2010. Two charts listing the iron catalysts and ligands/additives used in the surveyed reactions precede the tables. The tables are organized by electrophiles in the order in which their reactions are discussed in the section on Scope and Limitations. The titles of the individual tables can be found in the Table of Contents and are not repeated here. Table 1B lists both carbocyclic and heterocyclic alkenyl electrophiles. Reactions of imino chlorides are listed together with those of acyl electrophiles in Table 3. Heteroaryl electrophiles are listed in Table 5, including those where the leaving group is attached to an annulated aromatic ring, whereas heterocyclic electrophiles in which the leaving group is attached to an sp^3-carbon are found in Table 13.

Products of coupling reactions under either oxidizing or reducing conditions are listed together with those of normal cross-coupling reactions in the appropriate tables; the reagents that do not fit the description in the table header are marked with an asterisk.

Electrophiles are listed in the order of increasing carbon count. To group similar electrophiles together, leaving groups, protecting groups, including carbon-bound silyl groups, and groups on nitrogen, oxygen, and sulfur such as in amines, amides, esters or ethers, are not counted unless they take part in the reaction. An em-dash (—) signifies that a yield or other parameter was not reported.

The following abbreviations that are not in the list of standard abbreviations published by the *Journal of Organic Chemistry* are used in the tables:

BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
bmim	1-butyl-3-methylimidazolium
(t-Bu)$_2$P(biphenyl)	di-*tert*-butylphosphino-4-biphenyl
bzac	benzoylacetonate
Cy$_2$P(MeO-biphenyl)	2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl
dbm	dibenzoylmethide
DMEDA	*N*,*N*′-dimethylethylenediamine
dmpe	1,2-bis(dimethylphosphino)ethane
dpm	dipivaloylmethide
dppb	1,4-bis(diphenylphosphino)butane
dppbz	1,2-bis(diphenylphosphino)benzene
dppe	1,2-bis(diphenylphosphino)ethane
dppen	1,2-bis(diphenylphosphino)ethylene
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
dppy	2-(diphenylphosphino)pyridine
Fe(+3) resin	a copolymer of Fe(2-acetoacetoxy)ethyl methacrylate with *N*,*N*-dimethylacrylamide
HMTA	hexamethylenetetramine
I-Adm•HBF$_4$	1,3-bis(1-adamantyl)imidazolium tetrafluoroborate
I-t-Bu•HCl	1,3-dibutylimidazolium chloride
I-MeBu•HBF$_4$	1-butyl-3-methylimidazolium tetrafluoroborate
IPr•HCl	1,3-bis(2,6-diisopropylphenyl)imidazolium chloride
Nf	nonaflate, $SO_2(CF_2)_3CF_3$
Np	naphthyl
PMP	4-methoxyphenyl
SIPr•HBF$_4$	1,3-bis(2,6-diisopropylphenyl)imidazolinium tetrafluoroborate
SIPr•HCl	1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride

sulfolane	2,3,4,5-tetrahydrothiophene-1,1-dioxide
TBDPS	*tert*-butyldiphenylsilyl
TEEDA	N,N,N',N'-tetraethylethylenediamine
TES	triethylsilyl
XantPhos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene

CHART 1. IRON CATALYSTS USED IN TABLES

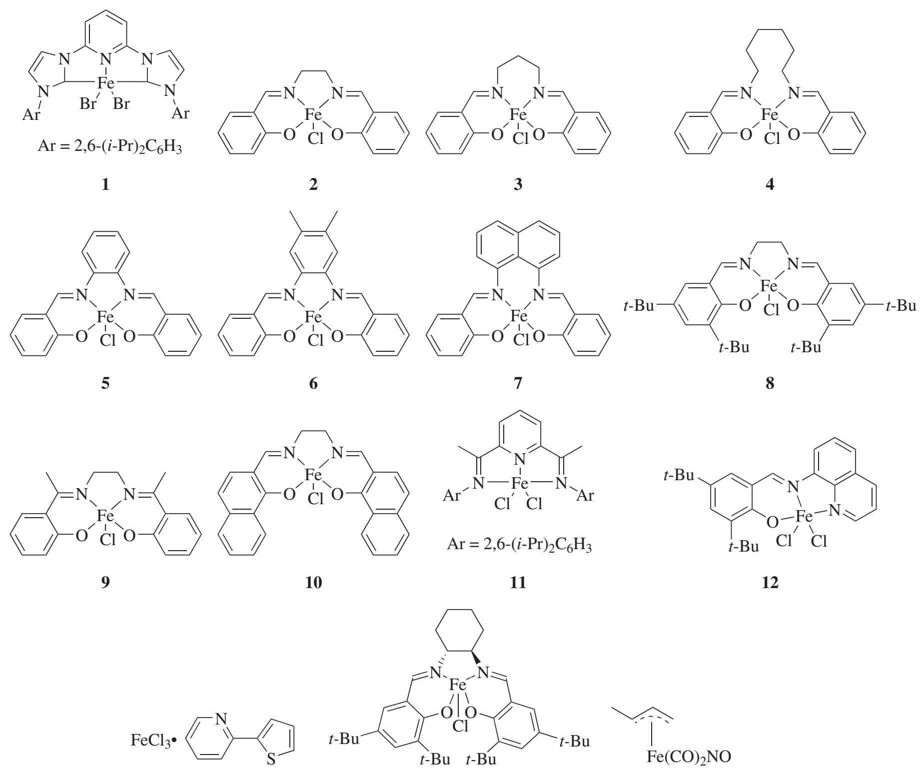
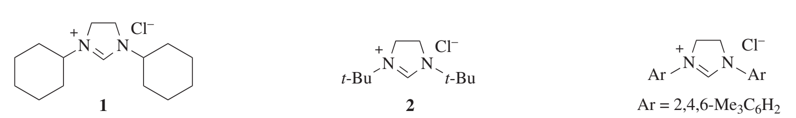
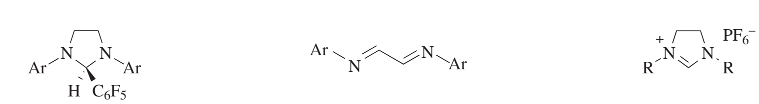


CHART 2. LIGANDS/ADDITIVES USED IN TABLES





	Ar
4	2,4,6-$Me_3C_6H_2$
5	2,6-(i-Pr)$_2C_6H_3$

	Ar
6a	2,4,6-$Me_3C_6H_2$
6b	2,6-(i-Pr)$_2C_6H_3$

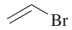
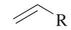
	R
7a	i-Pr
7b	t-Bu
7c	2,4,6-$Me_3C_6H_2$
7d	Ph_2CH

TABLE 1A. REACTION OF ACYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

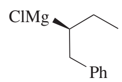
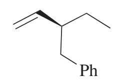
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

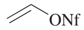
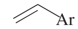
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

C_2

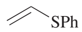
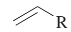
 RMgBr — $FeCl_3$ (*x* mol %) — 

R	*x*	Solvent	Temp		Refs.
n-Pr	—	—	—	(—)	5, 51
n-C_6H_{13}	0.125	THF	0°	(83)	5, 51
CH_2=$CH(CH_2)_4$	0.167	THF	rt	(64)	5

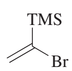
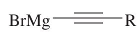
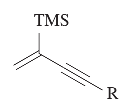
 — $FeCl_3$ (10 mol %), THF, –78°, 5 d —  (35) er 76.5:23.5 — 45

 ArCu(CN)MgCl — $Fe(acac)_3$ (10 mol %), DMF, rt, 0.5 h —  — 77

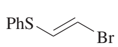
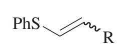
Ar	
3-BrC_6H_4	(62)
4-$EtO_2CC_6H_4$	(64)
1-Np	(71)

 RMgBr — $Fe(acac)_3$ (5 mol %), THF, rt, 17–22 h —  **I** + PhR **II** — 74

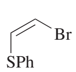
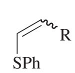
R	**I**	**II**
2-$MeOC_6H_4$	(11)	(—)
3-$MeOC_6H_4$	(40)	(—)
4-$MeOC_6H_4$	(74)	(2)
n-$C_{12}H_{25}$	(65)	(—)
4-$MeC_6H_4C{\equiv}C$	(0)	(—)

  — $FeCl_3$ (*x* mol %), LiBr (1.2 eq), THF, 60° —  — 67

R	*x*	Time (h)	
TBS	3	24	(87)
TIPS	0.5	24	(84)
TBDPSO$(CH_2)_2$	1	24	(88)
Ph	0.5	24	(91)
n-C_6H_{13}	1	12	(>99)

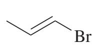
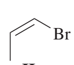
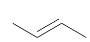
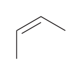
 RMgCl — Catalyst (0.66 mol %), THF, –78° to rt, 12 h —  — 76

R	Catalyst		(*E*)/(*Z*)
i-Pr	$Fe(dbm)_3$	(60)	94.3:5.7
i-Pr	$Fe(dpm)_3$	(80)	100:0
s-Bu	$Fe(dbm)_3$	(76)	100:0
s-Bu	$Fe(dpm)_3$	(71)	95:5

 RMgCl — Catalyst (0.66 mol %), THF, –78° to rt —  — 76

R	Catalyst	Time (h)		(*E*)/(*Z*)
i-Pr	$Fe(dbm)_3$	8	(50)	3.2:96.8
i-Pr	$Fe(dpm)_3$	8	(55)	0:100
s-Bu	$Fe(dbm)_3$	9	(45)	2.6:97.4
s-Bu	$Fe(dpm)_3$	9	(46)	3.3:96.7

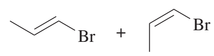
C_3

 **I** +  **II** MeMgX — Catalyst (*x* mol %), additive (*y* eq), THF —  **III** +  **IV**

I/II	X	Catalyst	*x*	Additive	*y*	Temp	Time (h)	**III + IV**	**III/IV**	Refs.
—	Cl	$Fe(acac)_3$	3	NMP	9	15–20°	0.25	(57)	—	54
—	Cl	$Fe(acac)_3$	3	sulfolane	9	15–20°	0.25	(82)	—	54
—	Br	$FeCl_3$	—	—	—	—	0.75	(89)	—	5
I only	Br	$FeCl_3$	0.06	—	—	rt	0.75	(—)	**III** only	5, 51
II only	Br	$FeCl_3$	0.06	—	—	rt	0.75	(—)	**IV** only	5, 51
—	Br	$FeCl_3$	0.34	—	—	rt	0.75	(25)	—	52
—	Br	$Fe(CO_2t\text{-Bu})_3$	0.34	—	—	rt	0.75	(73)	—	52
—	Br	$Fe(acac)_3$	0.34	—	—	rt	0.75	(90)	—	52
—	Br	$FeCl_3(PPh_3)$	0.34	—	—	rt	0.75	(27)	—	52
—	Br	$Fe(CF_3COCHCOCF_3)_3$	0.34	—	—	rt	0.75	(25)	—	52
—	Br	$Fe(acac)Cl_2$	0.34	—	—	rt	0.75	(57)	—	52
—	Br	$Fe(acac)_2Cl$	0.34	—	—	rt	0.75	(>99)	—	52
—	Br	$Fe(dpm)_3$	0.34	—	—	rt	0.75	(>99)	—	52
—	Br	$Fe(dbm)_3$	0.34	—	—	rt	0.75	(>99)	—	52

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

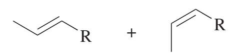
C_3



I + II

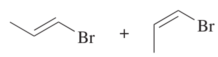
RMgBr

Fe(dbm)$_3$ (x mol %), THF, rt



III + IV

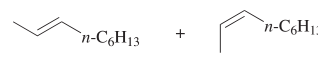
I/II	R	x	Time (h)	III + IV	III/IV	Refs.
—	Et	0.33	0.75	(58)[a]	—	52
I only	Et	0.3	1	(30)	III only	35
II only	Et	0.3	1	(5)	IV only	35
95:5	Et	0.3–0.4	1	(29–55)	—	35
95:5	Et	0.3	1	(49)	89:11	35
95:5	n-Pr	0.3	1	(73)	97:3	35
—	i-Pr	0.33	0.75	(60)[a]	—	52
95:5	i-Pr	0.3	1	(82)	—	35
95:5	i-Bu	0.3	1.5	(79)	III only	35
95:5	s-Bu	0.3	1.5	(77)	71:29	35
—	t-Bu	0.33	0.75	(27)	—	52
95:5	t-Bu	0.3	1	(60)	71:29	35
95:5	n-C_5H_{11}	0.3	1	(60)	—	35
95:5	2-pentyl	0.3	1	(75)	71:29	35



I + II, I/II = 95:5

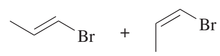
n-C_6H_{13}MgBr

FeCl$_3$ (0.125 mol %), THF, rt



III + IV

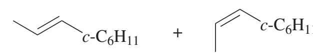
III + IV (67), III/IV = 47:53 — Refs. 5, 51



I + II

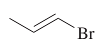
c-C_6H_{11}MX

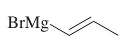
Catalyst (x mol %), additive, THF, rt



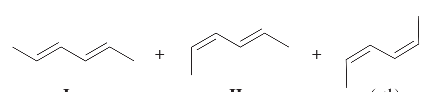
III + IV

M	X	I/II	Catalyst	x	Additive	Time (h)	III + IV	III/IV	Refs.
Mg	Br	—	Fe(dbm)$_3$	0.33	—	0.75	(54[a], 45)	—	52
Mg	Br	95:5	Fe(dbm)$_3$	0.3	—	1	(76)	79:21	35
Mn	Cl	—	Fe(acac)$_3$	3	NMP	1	(84)	—	62, 63



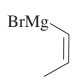


Fe(dbm)$_3$ (0.3 mol %), THF, rt, 1.5 h

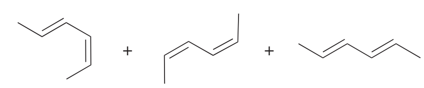


I + II + (<1)

I + II (30), I/II = 78:22 — Ref. 35



Fe(dbm)$_3$ (0.3 mol %), THF, rt, 1.5 h

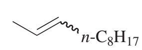


I + II + (<1)

I + II (26), I/II = 32:68 — Ref. 35

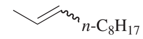
n-C_8H_{17}MX

Catalyst (x mol %), additive (y eq), THF

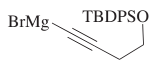
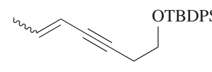
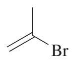
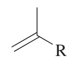


M	X	Catalyst	x	Additive	y	Temp (°)	Time (h)	Yield	Refs.
Mg	Br	Fe(acac)$_3$	3	—	—	–5 to 0	0.25	(40)	54
Mg	Br	Fe(acac)$_3$	3	NMP	2	–5 to 0	0.25	(87)	54
Mg	Br	Fe(acac)$_3$	3	NMP	9	–5 to 0	0.25	(87)	54
Mg	Br	Fe(acac)$_3$	3	DMPU	9	–5 to 0	0.25	(80)	54
Mg	Br	Fe(acac)$_3$	3	DMF	9	–5 to 0	0.25	(81)	54
Mg	Br	Fe(acac)$_3$	3	DMA	9	–5 to 0	0.25	(80)	54
Mg	Br	Fe(acac)$_3$	3	EtOCO$_2$Et	9	–5 to 0	0.25	(78)	54
Mg	Br	Fe(acac)$_3$	3	sulfolane	9	–5 to 0	0.25	(72)	54
Mg	Br	Fe(acac)$_3$	3	Et$_2$NCO$_2$Et	9	–5 to 0	0.25	(56)	54
Mg	Br	Fe(acac)$_3$	3	DME	9	–5 to 0	0.25	(59)	54
Mg	Br	Fe(dbm)$_3$	3	NMP	9	–5 to 0	0.25	(87)	54
Mg	Br	Fe(dbm)$_3$	3	NMP	9	–5 to 0	0.25	(88)	54

TABLE 1A. REACTION OF ACYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

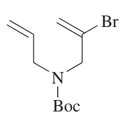
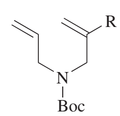
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3  *Continued from previous page.*	n-$C_8H_{17}MX$	Catalyst (x mol %), additive (y eq), THF		

M	X	Catalyst	x	Additive	y	Temp (°)	Time (h)		Refs.
Mg	Br	$FeCl_3$	3	NMP	9	–5 to 0	0.25	(88)	54
Mg	Br	$Fe(SO_4)_3$	3	NMP	9	–5 to 0	0.25	(31)	54
Mg	Br	$Fe(acac)_3$	1	NMP	9	–5 to 0	0.25	(87)	54
Mg	Br	$Fe(acac)_3$	0.1	NMP	9	–5 to 0	0.25	(88)	54
Mg	Br	$Fe(acac)_3$	0.01	NMP	9	–5 to 0	0.25	(82)	54
Mn	Cl	$Fe(acac)_3$	3	NMP	—	rt	1	(80)	62, 63

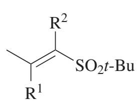
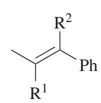
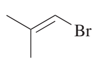
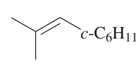
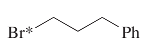
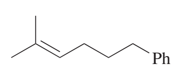
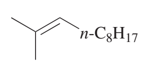
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 **I**		$FeCl_3$ (1 mol %), LiBr (1.2 eq), THF, 60°, 24 h	 **II**	67
	PhMnCl	$Fe(acac)_3$ (3 mol %), NMP, THF, rt, 1 h	 (71)	62, 63
	RMgX	Catalyst (1 mol %), additive (x eq), THF		

I (*E*)/(*Z*)		**II** (*E*)/(*Z*)
>99:1	(92)	93:7
<1:99	(92)	35:65

R	X	Catalyst	Additive	x	Temp (°)	Time (h)		Refs.
n-$C_6H_{13}C\equiv C$	Br	$FeCl_3$	LiBr	1.2	60	24	(76)	67
$PhC\equiv C$	Br	$FeCl_3$	LiBr	1.2	80	24	(60)	67
n-C_8H_{17}	Cl	$Fe(acac)_3$	NMP	9	–5 to 0	0.25	(86)	54

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgCl (x eq)	$Fe(acac)_3$ (2 mol %), THF/NMP, 0°, 30 min		180

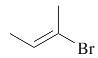
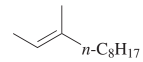
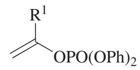
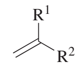
R	x	
i-Pr	—	(59)
n-Bu	—	(64)
t-Bu	—	(0)
Ph	2	(37)
Ph	3	(61)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	PhMgBr	$Fe(acac)_3$ (1 mol %), THF, rt, 20 h		16
	c-$C_6H_{11}MgCl$	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, –5 to 0°, 15 min	 (82)	54
		$FeCl_3$ (5 mol %), TMEDA (1.2 eq), Mg (1.2 eq), THF, 0°, 3 h	 (52)	145
	n-$C_8H_{17}MnCl$ (x eq)	Catalyst (y mol %), rt, 1 h		

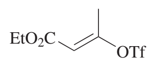
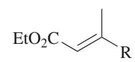
R^1	R^2	
Me	H	(50)
H	Me	(60)

x	Catalyst	y	Solvent		Refs.
1.05	$Fe(acac)_3$	3	THF	(12)	62, 63
1.05	$Fe(acac)_3$	3	DME	(12)	63
1.05	$Fe(acac)_3$	3	THF/AcOEt	(13)	63
1.05	$Fe(acac)_3$	3	THF/MeCN	(15)	63
1.05	$Fe(acac)_3$	3	THF/sulfolane	(24)	63
1.05	$Fe(acac)_3$	1	THF/NMP	(62)	63
1.05	$Fe(acac)_3$	3	THF/NMP	(76)	62, 63
1.05	$Fe(acac)_3$	6	THF/NMP	(76)	63
1.05	$Fe(dbm)_3$	3	THF/NMP	(70)	62, 63
1.05	$FeCl_3$	3	THF/NMP	(67)	62, 63
1.05	**13**	3	THF/NMP	(77)	63
1.4	$Fe(acac)_3$	3	THF/NMP	(90)	62, 63

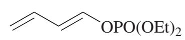
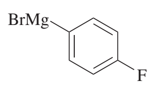
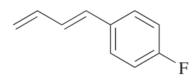
TABLE 1A. REACTION OF ACYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

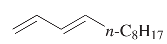
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	n-$C_8H_{17}MgCl$	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, –5 to 0°, 0.25 h	 (84)	54
$C_{4–6}$				
	R^2MgX	$Fe(acac)_3$ (3 mol %), NMP (9 eq), THF, –20°, 1.5 h		72

R^1	R^2	X	
Et	c-C_6H_{11}	Cl	(20)
Et	n-C_8H_{17}	Br	(82)
t-Bu	n-C_8H_{17}	Cl	(75)

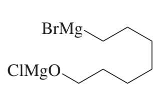
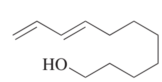
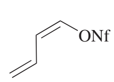
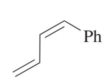
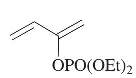
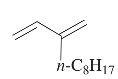
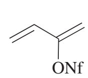
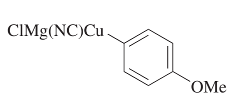
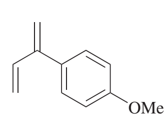
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	RMgBr	$Fe(acac)_3$ (x mol %), additive, THF, –30°		

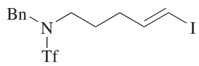
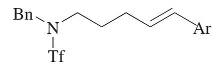
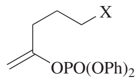
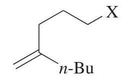
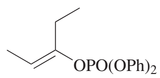
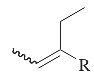
R	x	Additive		Refs.
MeC≡C$(CH_2)_2$	10	—	(97)	73, 148
Ph	7	NMP	(83)	73
4-$MeOC_6H_4$	10	NMP	(51)	73
n-$C_{14}H_{29}$	7	NMP	(98)	73

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 (E)/(Z) = 99:1		$Fe(acac)_3$ (1 mol %), THF, 20°, 0.5 h (slow add.)	 (52), (E)/(Z) = 80:20	58

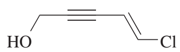
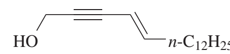
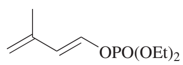
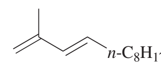
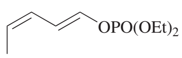
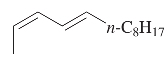
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	n-$C_8H_{17}MgCl$	$Fe(acac)_3$ (x mol %), (slow add.)	 (E)/(Z) = 98:2	58

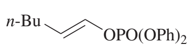
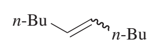
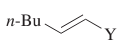
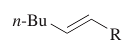
x	Solvent	Temp (°)	Time (min)	
1	THF/NMP	–20	10	(54)
1	THF	–20	10	(82)
1	Et_2O	–20	10	(75)
1	DME	–20	10	(79)
5	THF	–20	10	(78)
0.5	THF	0	10	(40)
1	THF	20	10	(86)
1	THF	40	10	(92)
1	THF	20	10	(91)
1	THF	20	20	(92)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (1 mol %), THF, 20°, 20 min (slow add.)	 (79), (E)/(Z) > 96:1	58
	PhCu(CN)MgCl	$Fe(acac)_3$ (10 mol %), DMF, rt, 1 h	 (41)	77
	n-$C_8H_{17}MgCl$	1. $Fe(acac)_3$ (1 mol %), THF, 20° 2. 20 min (slow add.) 3. 15 min	 (61)	58
		$Fe(acac)_3$ (10 mol %), DMF, rt, 1 h	 (—)	77

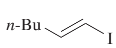
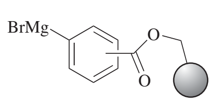
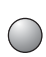
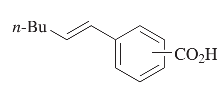
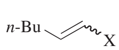
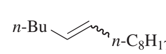
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	ArMgBr	$Fe(acac)_3$ (0.5 mol %), THF, –20°	 Ar: Ph (65); 4-$EtO_2CC_6H_4$ (69)	70
	*n*-BuMgBr	$Fe(acac)_3$ (3 mol %), NMP (9 eq), THF, –5 to 0°, 1.5 h	 X: Cl (90); Br (0)	72
 **I**	RMgX	$Fe(acac)_3$ (*x* mol %), DMPU (9 eq), THF, –20°	 **II**	72

I (*E*)/(*Z*)	R	X	*x*	Time (h)		**II** (*E*)/(*Z*)
71:29	Ph	Br	3	1.5	(73)	93:7
71:29	*n*-C_8H_{17}	Cl	3	1.5	(81)	83:17
68:32	*n*-C_8H_{17}	Br	4	0.5	(81)	>99:1

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	*n*-$C_{12}H_{25}$MgBr	$Fe(acac)_3$ (3 mol %), THF/NMP, 0°	 (85)	60
 (*E*)/(*Z*) = 96:4	*n*-C_8H_{17}MgCl	1. $Fe(acac)_3$ (1 mol %), THF, 20° 2. 20 min (slow add.) 3. 15 min	 (85), (*E*)/(*Z*) = 90:10	58
 C1–C2: (*E*)/(*Z*) > 99:1 C3–C4: (*E*)/(*Z*) = 7:93	*n*-C_8H_{17}MgCl	1. $Fe(acac)_3$ (1 mol %), THF, 20° 2. 20 min (slow add.) 3. 15 min	 (90) C1–C2: (*E*)/(*Z*) > 99:1 C3–C4: (*E*)/(*Z*) = 7:93	58

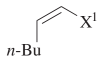
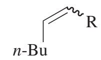
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
 (*E*)/(*Z*) = 70:30	*n*-BuMgCl (*x* eq)	$Fe(acac)_3$ (3 mol %), THF, –20°, 1 h	 *x* = 0.85: (56), (*E*)/(*Z*) 91:9; *x* = 1.2: (71), (*E*)/(*Z*) 91:9	72
	RMX	Catalyst (*x* mol %), additive (*y* eq)		

Y	R	M	X	Catalyst	*x*	Additive	*y*	Solvent	Temp	Time (h)		(*E*)/(*Z*)	Refs.
Br	Ph	Mg	Br	$Fe(dbm)_3$	0.5	—	—	DME	–20° to rt	2	(65)	—	53
I	Ph	Mg	Br	$Fe(dbm)_3$	0.5	—	—	DME/Et_2O	–20° to rt	2	(77)[a]	—	53
$(PhO)_2PO_2$	Ph	Mg	Cl	$Fe(acac)_3$	3	NMP	9	THF	–20°	1.5	(81)	85:15	72
I	3-FC_6H_4	Mn	Br	$Fe(acac)_3$	3	—	—	THF	rt	—	(67)	—	179a
I	3-$NfOC_6H_4$	Mg	Br	$Fe(acac)_3$	0.5	—	—	THF	–20°	—	(50)	—	70
I	4-NCC_6H_4	Mg	Br	$Fe(acac)_3$	0.5	—	—	THF	–20°	—	(60)	—	70
I	4-$EtO_2CC_6H_4$	Mg	Br	$Fe(acac)_3$	0.5	—	—	THF	–20°	—	(60)	—	70
I	3-EtO_2C-4-$NfOC_6H_3$	Mg	Br	$Fe(acac)_3$	0.5	—	—	THF	–20°	—	(73)	—	70

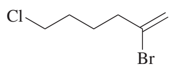
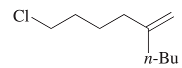
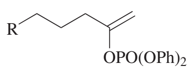
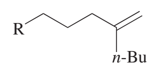
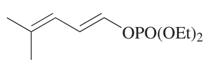
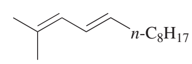
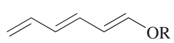
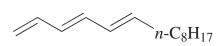
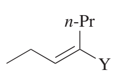
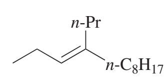
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	  = Wang resin	1. $Fe(acac)_3$ (5 mol %), THF, –20°, 0.5 h 2. TFA/CH_2Cl_2/H_2O (9:1:1), rt, 0.25 h	 Isomer: 3- (90); 4- (94)	70
 **I**	*n*-C_8H_{17}MCl	$Fe(acac)_3$ (*x* mol %), NMP (*y* eq), THF	 **II**	

I (*E*)/(*Z*)	X	M	*x*	*y*	Temp	Time (h)		**II** (*E*)/(*Z*)	Refs.
mix	Cl	Mn	3	—	rt	1	(88)	mix	62, 63
mix	Br	Mn	3	—	rt	1	(89)	mix	62, 63
(*E*) only	I	Mg	0.1	2	–5 to 0°	0.25	(75)	(*E*) only	54
(*E*) only	I	Mn	3	—	rt	1	(88)	>98:2	62, 63

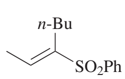
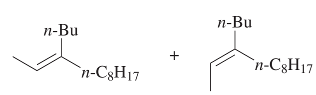
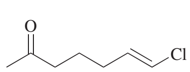
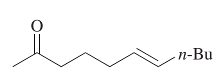
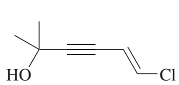
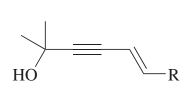
TABLE 1A. REACTION OF ACYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	RMX^2	Catalyst (*x* mol %), additive (*y* eq)		

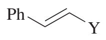
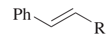
X^1	R	M	X^2	Catalyst	*x*	Additive	*y*	Solvent	Temp	Time (h)		(*Z*)/(*E*)	Refs.
Br	Ph	Mg	Br	$Fe(dbm)_3$	0.5	—	—	DME	–20° to rt	2	(83)[a]	2:1	53
I	Ph	Mg	Br	$Fe(dbm)_3$	0.5	—	—	DME/Et_2O	–20° to rt	2	(93)[a]	1:2	53
Br	*c*-C_6H_{13}	Mg	Cl	$Fe(acac)_3$	1	NMP	9	THF	–5 to 0°	0.25	(89)	(*Z*) only	54
I	*n*-C_8H_{17}	Mg	Cl	$Fe(acac)_3$	0.1	NMP	2	THF	–5 to 0°	0.25	(84)	(*Z*) only	54
I	*n*-C_8H_{17}	Mn	Cl	$Fe(acac)_3$	3	NMP	—	THF	rt	1	(90)	>98:2	62, 63

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	*n*-BuMgCl	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, –5 to 0°, 0.25 h	 (79)	54
	*n*-BuMgBr	$Fe(acac)_3$ (3 mol %), NMP (9 eq), THF, –5 to 0°, 1.5 h	 R: NC (96); MeO_2C (84)	72
 (*E*)/(*Z*) > 99:1	*n*-C_8H_{17}MgCl	1. $Fe(acac)_3$ (1 mol %), THF, 20° 2. 20 min (slow add.) 3. 15 min	 (93), (*E*)/(*Z*) = 99:1	58
 R = $(PhO)_2OP$ (*E*)/(*Z*) > 99:1	*n*-C_8H_{17}MgCl	1. $Fe(acac)_3$ (1 mol %), THF, 20° 2. 20 min (slow add.) 3. 15 min	 (88), (*E*)/(*Z*) = 99:1	58
C_7				
 **I**	*n*-C_8H_{17}MgX	$Fe(acac)_3$ (*x* mol %), additive (9 eq), THF, –20°	 **II**	72

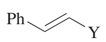
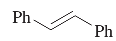
I (*E*)/(*Z*)	Y	X	*x*	Additive	Time (h)		**II** (*E*)/(*Z*)
60:40	Br	Br	3	NMP	1	(50)	74:26
70:30	$(PhO)_2PO_2$	Cl	3	DMPU	1.5	(75)	88:12
70:30	$(PhO)_2PO_2$	Br	4	DMPU	0.5	(86)	>98:2

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	*n*-C_8H_{17}MgBr	$Fe(acac)_3$ (1 mol %), THF, rt, 20 h	 **I** **II** **I** + **II** (63), **I**/**II** = 97:3	16
	*n*-BuMgCl	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, –5 to 0°, 0.25 h	 (80)	54
	RMgX	$Fe(acac)_3$ (3 mol %), THF/NMP, 0°		60

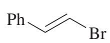
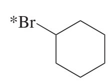
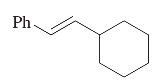
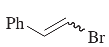
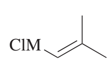
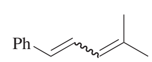
R	X	
Me	Br	(70)
Et	Br	(73)
i-Pr	Cl	(75)
t-Bu	Br	(65)
c-C_6H_{11}	Br	(61)
n-$C_{12}H_{25}$	Br	(88)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
 **I**	RMX	Catalyst (*x* mol %), additive (*y* eq), THF	 **II**	

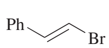
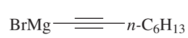
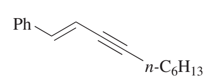
I (*E*)/(*Z*)	Y	R	M	X	Catalyst	*x*	Additive	*y*	Temp	Time (h)		**II** (*E*)/(*Z*)	Refs.
(*E*) only	Br	Me	Mg	Cl	$Fe(acac)_3$	1	NMP	9	15–20°	0.25	(88)	(*E*) only	54
(*E*) only	Br	Et	Mg	Br	$Fe(dbm)_3$	0.33	none	—	rt	0.75	(59)[a]	(*E*) only	52
(*E*) only	Br	*i*-Pr	Mg	Cl	$Fe(acac)_3$	1	NMP	9	–5 to 0°	0.25	(73)	(*E*) only	54
(*E*) only	Br	*n*-Bu	Mg	Cl	$Fe(acac)_3$	1	NMP	9	–5 to 0°	0.25	(84)	(*E*) only	54
mix	Br	*n*-Bu	Mn	Cl	$Fe(acac)_3$	3	none	—	rt	1	(64)	mix	63
mix	Br	*n*-Bu	Mn	Cl	$Fe(acac)_3$	3	NMP	—	rt	1	(87)	mix	62, 63
84:16	$(PhO)_2PO_2$	*n*-Bu	Mg	Cl	$Fe(acac)_3$	3	none	—	–20°	1.5	(87)	90:10	72
(*E*) only	Br	*t*-Bu	Mg	Cl	$Fe(acac)_3$	1	NMP	9	–5 to 0°	0.25	(64)	(*E*) only	54
mix	Br	*t*-Bu	Mn	Cl	$Fe(acac)_3$	3	NMP	—	rt	1	(30)	mix	62, 63
2:1	PivO	*n*-C_6H_{13}	Mg	Cl	$FeCl_2$	1	**3**	2 mol %	0°	1	(71)	2:1	68
(*E*) only	ClO_2S[b]	*n*-C_6H_{13}	Mg	Br	$Fe(acac)_3$	5	NMP	—	80°	2	(68)	(*E*) only	61
(*E*) only	ClO_2S[b]	*n*-C_8H_{17}	Mg	Br	$Fe(acac)_3$	5	NMP	—	80°	2	(61)	(*E*) only	61

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgX	Catalyst (*x* mol %)		

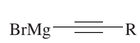
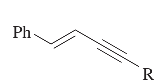
Y	X	Catalyst	*x*	Solvent	Temp	Time (h)		Refs.
Br	Cl	$Fe(acac)_3$	1	THF/NMP	5–20°	0.33	(90)	54
Br	Br	$Fe(dbm)_3$	0.33	THF	rt	0.75	(32)	52, 53
Br	Br	$Fe(dbm)_3$	0.5	DME/Et_2O	–20° to rt	2	(90[a], 68)	53
Br	Br	$Cp(MeP_2Ph)_2FeBr$	5	Et_2O	rt	24	(84)	95
ClO_2S	Br	$Fe(acac)_3$	5	THF/NMP	80°	2[b]	(55)	61

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (5 mol %), TMEDA (1.2 eq), Mg (1.2 eq), THF, 0°, 3 h	 (5)	145
 **I**		$Fe(acac)_3$ (*x* mol %), additive, THF	 **II**	

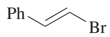
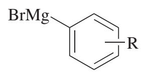
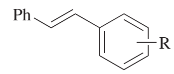
I (*E*)/(*Z*)	M	*x*	Additive	Temp	Time (h)		**II** (*E*)/(*Z*)	Refs.
(*E*) only	Mg	1	none	15–20°	—	(60)	(*E*) only	54
mix	Mn	3	NMP	rt	1	(25)	mix	62, 63

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 (*E*)/(*Z*) = 85:15		Catalyst (0.5 mol %), additive, THF, 24 h	 (*E*)/(*Z*) = 88:12	67

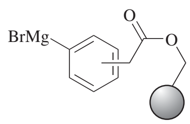
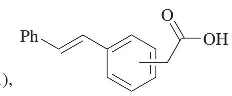
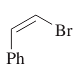
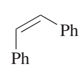
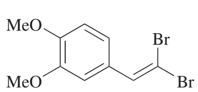
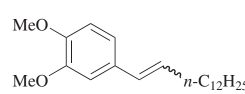
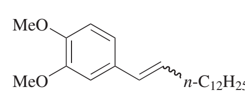
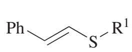
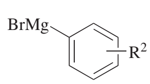
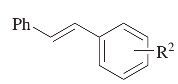
Catalyst	Additive	Temp (°)	
$FeCl_3$	none	50	(12)
$FeCl_3$	NMP (9 eq)	50	(2)
$FeCl_3$	HMTA (5 mol %), TMEDA (10 mol %)	50	(15)
$FeCl_3$	SIPr•HCl (2 mol %)	50	(11)
$FeCl_3$	PCy_3 (1 mol %)	50	(17)
$FeCl_3$	TMEDA (1.2 eq)	50	(60)
$FeCl_3$	LiCl (1.2 eq)	50	(82)
$FeCl_3$	LiBr (1.2 eq)	50	(85)
$FeCl_3$	LiBr (0.6 eq)	50	(27)
$FeCl_3$	LiBr (0.2 eq)	50	(21)
$FeCl_3$	$MgBr_2$ (1.2 eq)	50	(28)
$FeCl_3$	$ZnCl_2$ (1.2 eq)	50	(1)
$FeCl_3$	LiBr (1.2 eq)	60	(95)
$FeCl_2$	LiBr (1.2 eq)	60	(89)
$Fe(acac)_3$	LiBr (1.2 eq)	60	(86)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (1 mol %), LiBr (1.2 eq), THF, 60°, 24 h		67

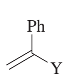
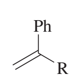
R		(*E*)/(*Z*)
$TBSO(Me)_2C$	(82)	92:8
$TBSO(CH_2)_2$	(91)	85:15

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		Catalyst (*x* mol %)		

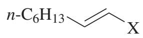
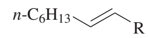
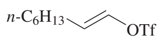
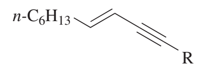
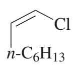
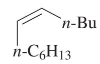
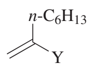
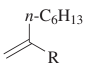
R	Catalyst	*x*	Solvent	Temp	Time (h)		Refs.
4-Cl	$Fe(dbm)_3$	0.5–1	DME/Et_2O	–20° to rt	2	(75)	53
3-MeO	$Fe(dbm)_3$	0.5–1	DME/Et_2O	–20° to rt	2	(75)[a]	53
3-NfO	$Fe(acac)_3$	0.5	THF	–20°	—	(62)	70
3-TIPS	$Fe(acac)_3$	0.5	THF	–20°	—	(62)	70
2-Me	$Fe(dbm)_3$	0.5–1	DME/Et_2O	–20° to rt	2	(100)[a]	53
2,4,6-Me_3	$Fe(dbm)_3$	0.5–1	DME/Et_2O	–20° to rt	2	(0)	53
1-Np	$Fe(dbm)_3$	0.5–1	DME/Et_2O	–20° to rt	2	(83[a], 56)	53

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	  = Wang Resin	1. $Fe(acac)_3$ (5 mol %), THF, –20°, 0.5 h 2. $TFA/CH_2Cl_2/H_2O$ (9:1:1), rt, 0.25 h	 Isomer: 3- (84); 4- (86)	70
	PhMgBr	$Fe(dbm)_3$ (0.5 mol %), DME/Et_2O, –20° to rt, 2 h	 (52)[a]	53
	*n*-$C_{12}H_{25}$MgBr **I** (1 eq)	1. $Fe(acac)_3$ (5 mol %), *i*-PrMgCl (1 eq), THF/NMP, –10 to 0°, 0.5 h 2. **I**, –10 to 0°, 3 h	 (44)	69
	n-$C_{12}H_{25}$MgBr (2 eq)	$Fe(acac)_3$ (5 mol %), THF/NMP, –10 to 0°, 3 h	 (45)	69
		$Fe(acac)_3$ (5 mol %), THF		74

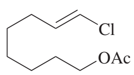
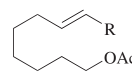
R[1]	R[2]	Temp	Time (h)	
2-pyrimidyl	H	rt	2	(43)
2-pyrimidyl	4-MeO	60°	—	(59)
Ph	4-MeO	60°	—	(31)

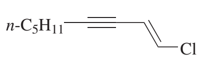
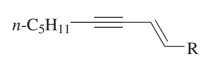
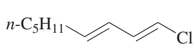
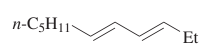
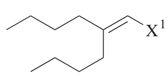
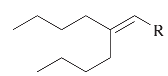
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgX	Catalyst (*x* mol %), additive (*y* eq)		

Y	R	X	Catalyst	*x*	Additive	*y*	Solvent	Temp	Time (h)		Refs.
Br	Me	Cl	$Fe(acac)_3$	1	NMP	9	THF	15–20°	0.25	(60)	54
$(PhO)_2PO_2$	*n*-Bu	Cl	$Fe(acac)_3$	3	none	—	THF	–20°	1.5	(90)	72
Br	Ph	Br	$Fe(dbm)_3$	0.5	none	—	DME/Et_2O	–20° to rt	2	(75)[a]	53

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	RMgCl	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, –5 to 0°, 0.25 h	 X R Cl *n*-Bu (75) Br *n*-Bu (64) I *n*-Bu (83) Cl *s*-Bu (74) I *s*-Bu (80) Br *t*-Bu (80)	54
	BrMg—≡—R	$FeCl_3$ (1 mol %), LiBr (1.2 eq), THF, 60°, 24 h	 R TBS (91) *n*-C_6H_{13} (75)	67
	*n*-BuMgCl	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, –5 to 0°, 0.25 h	 (80)	54
	RMgX	$Fe(acac)_3$ (*x* mol %), NMP (9 eq), THF		

Y	R	X	*x*	Temp (°)	Time (h)		Refs.
Br	*i*-Pr	Cl	1	–5 to 0	0.25	(72)	54
$(PhO)_2PO_2$	*n*-Bu	Br	3	–20	1.5	(75)	72

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgCl	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, –5 to 0°, 0.25 h	 R *i*-Pr (72) *n*-Bu (80)	54

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	RMgBr	$Fe(acac)_3$ (3 mol %), THF/NMP, 0°	 R *c*-C_6H_{11} (74) *n*-$C_{12}H_{25}$ (68)	60
	EtMgBr	$Fe(acac)_3$ (3 mol %), THF/NMP, 0°	 (79)	60
C_{10}				
	$RMgX^2$	$Fe(acac)_3$ (*x* mol %), additive (*y* eq), THF		

X^1	R	X^2	*x*	Additive	*y*	Temp (°)	Time (h)		Refs.
I	Me	Cl	1	NMP	9	15–20	0.25	(75)	54
Cl	*n*-Bu	Cl	1	none	—	–5 to 0	0.25	(5)	54
Cl	*n*-Bu	Cl	1	NMP	9	–5 to 0	0.25	(85)	54
Cl	*n*-Bu	Br	3	none	—	–20	1.5	(14)	72
Cl	*n*-Bu	Br	3	NMP	9	–20	1.5	(85)	72
Cl	*n*-Bu	Br	3	$(EtO)_3PO$	9	–20	1.5	(88)	72
Br	*n*-Bu	Cl	0.1	NMP	2	–5 to 0	0.25	(55)	54
Br	*n*-Bu	Cl	1	NMP	2	–5 to 0	0.25	(82)	54
I	*n*-Bu	Cl	1	NMP	2	–5 to 0	0.25	(83)	54
Cl	*c*-C_6H_{11}	Cl	1	NMP	9	–5 to 0	0.25	(87)	54

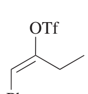
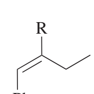
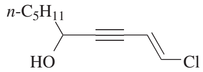
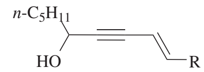
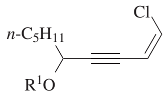
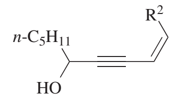
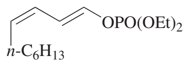
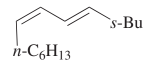
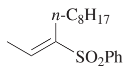
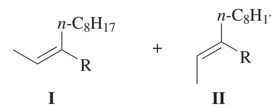
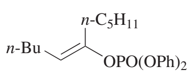
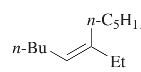
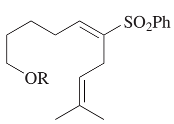
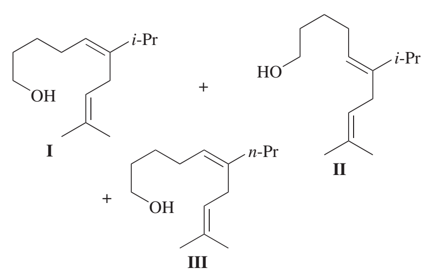
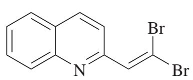
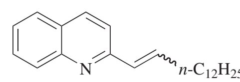
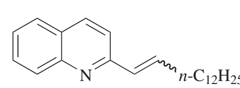
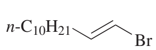
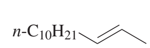
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, –30°	 R Me (87) *n*-Bu (90) 4-$MeOC_6H_4$ (84)	73

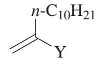
TABLE 1A. REACTION OF ACYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	RMgBr	$Fe(acac)_3$ (3 mol %), THF/NMP, 0°	 R c-C_6H_{11} (72) n-$C_{12}H_{25}$ (76)	60
	R^2MgBr	$Fe(acac)_3$ (3 mol %), NMP (*y* eq), THF	 R^1 / R^2 / *y* / Temp (°) / Time (h) Ac / Et / 15 / –10 to 0 / 1 / (58) H / c-C_6H_{11} / — / 0 / — / (82) H / n-$C_{12}H_{25}$ / — / 0 / — / (74)	60
 C1–C2: (*E*)/(*Z*) > 99:1 C3–C4: (*E*)/(*Z*) = 57:43	s-BuMgCl	1. $Fe(acac)_3$ (1 mol %), THF, 20° 2. 20 min (slow add.) 3. 15 min	 (78) C1–C2: (*E*)/(*Z*) > 99:1 C3–C4: (*E*)/(*Z*) = 60:40	58
C_{11}				
	RMgBr	$Fe(acac)_3$ (1 mol %), THF, rt, 20 h	 **I** + **II** R / **I** / **II** / **I + II** i-Pr / (—) / (—) / (3)[c] n-Bu / (2) / (61) / (—)	16

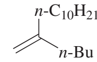
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 (*E*)/(*Z*) = 69:31	EtMgBr (*x* eq)	$Fe(acac)_3$ (4 mol %), DMPU (9 eq), THF, –20°, 0.5 h	 *x* / / (*E*)/(*Z*) 0.72 / (68) / 2:98 0.83 / (91) / 7:93	72
	i-PrMgBr	1. $FeCl_3$ (3 mol %), Et_2O, 20°, 1 h 2. Hydrolysis R / **I + II** / **I/II** / **III** Ac / (17) / 98:2 / (0.3) TBS / (36) / 98:2 / (0.5) Ph_3C / (32) / 92:8 / (0.3)	 **I** + **II** + **III**	59
	n-$C_{12}H_{25}$MgBr **I** (1 eq)	1. $Fe(acac)_3$ (5 mol %), i-PrMgCl (1 eq), THF/NMP, –10 to 0°, 0.5 h 2. **I**, –10 to 0°, 3 h	 (63)	69
	n-$C_{12}H_{25}$MgBr (*x* eq)	$Fe(acac)_3$ (5 mol %), THF/NMP, –10 to 0°	 *x* / Time (h) 1.1 / 0.5 / (15) 2 / 3 / (45)	69
C_{12}				
	MeMgCl	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, 15–20°, 0.25 h	 (87)	54

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

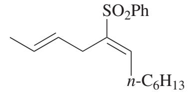
C_{12}



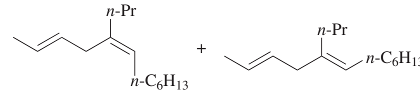
n-BuMCl — Fe(acac)$_3$ (x mol %), NMP (y eq), THF



Y	M	x	y	Temp	Time (h)		Refs.
(EtO)$_2$PO$_2$	Mg	6	9	–5 to 0°	0.25	(78)	54
Br	Mn	3	—	rt	1	(89)	62, 63



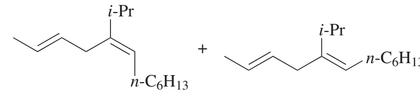
n-PrMgBr — FeCl$_3$ (3 mol %), Et$_2$O, 20°, 16 h



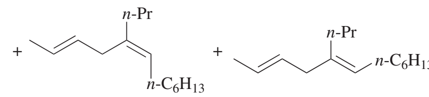
I **II**

I + II (60), **I/II** = 98:2 — 59

i-PrMgBr — Catalyst (x mol %), additive (3 mol %), 20°, 16 h



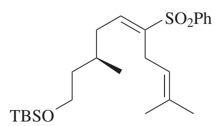
I **II**



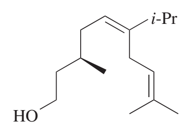
III **IV**

59

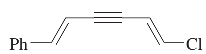
Catalyst	x	Additive	Solvent	I + II	I/II	III + IV
Fe(dbm)$_3$	3	—	THF	(5)	—	(0)
Fe(dbm)$_3$	3	—	Et$_2$O	(10)	97:3	(0)
Fe(acac)$_3$	3	—	Et$_2$O	(27)	97:3	(1)
Fe(acac)$_3$	3	(n-Bu)$_3$P	Et$_2$O	(6)	—	(8)
FeCl$_3$	3	—	THF	(8)	98:2	(0)
FeCl$_3$	2	—	Et$_2$O	(28)	98:2	(0)



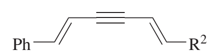
i-PrMgBr — 1. FeCl$_3$, (3 mol %), Et$_2$O, 20°, 3 h 2. TBAF, 0°, 2 h



(36) — 185



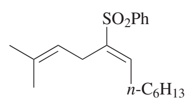
R^{1}MgX — Fe(acac)$_3$ (3 mol %), THF/NMP



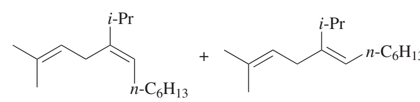
60

R^1	X	R^2	Temp (°)	Time (h)	
Et	Br	Et	–10 to 0	1	(66)
c-C$_6$H$_{11}$	Br	c-C$_6$H$_{11}$	0	—	(76)
n-C$_{12}$H$_{25}$	Br	n-C$_{12}$H$_{25}$	0	—	(71)
ClMgO(CH$_2$)$_3$	Cl	HO(CH$_2$)$_3$	0	—	(63)

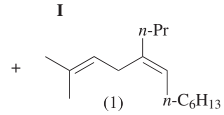
C_{13}



i-PrMgBr — FeCl$_3$ (3 mol %), Et$_2$O, 20°, 1 h

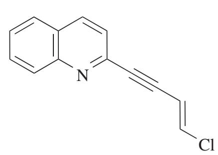


I **II**

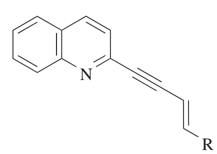


(1)

I + II (32), **I/II** = 98:2 — 59

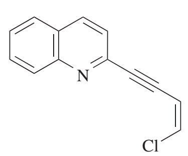


RMgCl — Fe(acac)$_3$ (3 mol %), NMP (15 eq), THF, –10°, 0.25 h; then 0°, 1 h

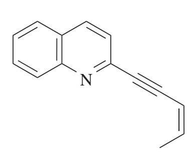


R	
Me	(25)
Et	(75)

60

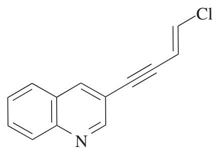
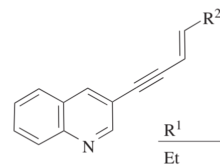
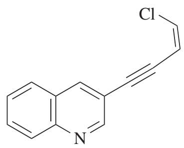
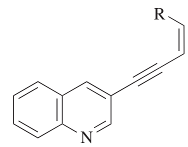
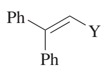
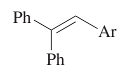
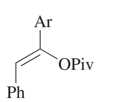
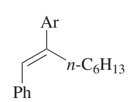
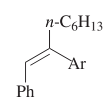


MeMgCl — Fe(acac)$_3$ (3 mol %), NMP (15 eq), THF, –10°, 0.25 h; then 0°, 1 h



(76) — 60

TABLE 1A. REACTION OF ACYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
	R^1MgCl	$Fe(acac)_3$ (3 mol %), NMP (15 eq), THF, –10°, 0.25 h; then 0°, 1 h	 R^1 / R^2 Et / Et (68) $ClMgO(CH_2)_3$ / $HO(CH_2)_3$ (36)	60
	RMgCl	$Fe(acac)_3$ (3 mol %), NMP (15 eq), THF, –10°, 0.25 h; then 0°, 1 h	 R Me (37) Et (70)	60
C_{14}				
	ArCu(CN)MCl	$Fe(acac)_3$ (10 mol %), DMF, rt, 1 h	 Y / Ar / M TfO / Ph / — (86) NfO / Ph / Mg (81) TfO / 2-MeC_6H_4 / — (59) TfO / 4-$MeOC_6H_4$ / — (78) TfO / 3-$CF_3C_6H_4$ / Mg (74) NfO / 3-NCC_6H_4 / Mg (56) TfO / 4-$EtO_2CC_6H_4$ / Mg (77)	77
	n-$C_6H_{13}MgCl$	$FeCl_2$ (1 mol %), ligand **3** (2 mol %), THF, rt, 2 h	 **I** +  **II** Ar / **I + II** / **I/II** Ph / (91) / 2:1 4-FC_6H_4 / (85) / 2:1 4-$MeOC_6H_4$ / (70) / 2:1	68

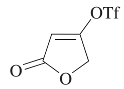
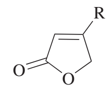
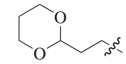
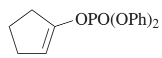
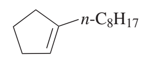
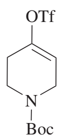
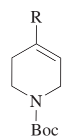
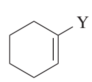
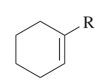
[a] The yield was determined by GLC.

[b] The nucleophile was added slowly at a rate of 2 mL/h.

[c] The configuration of the product was not reported.

TABLE 1B. REACTION OF CYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	RMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, –30°	 R: Me (70) $TMSCH_2$ (80) Ph (51) n-C_6H_{13} (68)  (67) 4-$MeOC_6H_4(CH_2)_2$ (84) n-$C_{14}H_{29}$ (66)	73
C_5				
	n-$C_8H_{17}MgBr$	$Fe(acac)_3$ (6 mol %), NMP (9 eq), THF, –20°, 3 h	 (82)	72
	RMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, –30°	 R: Ph (47) n-$C_{14}H_{29}$ (73)	73
C_6				
	RMX	$Fe(acac)_3$ (x mol %), additive (y eq), THF		

Y	R	M	X	x	Additive	y	Temp	Time (h)		Refs.
Cl	n-Bu	Mg	Cl	1	NMP	9	–5 to 0°	0.25	(75)	54
Cl	n-Bu	Mn	Cl	3	NMP	—	rt	1	(80)	62, 63
TfO	n-Bu	Mg	Br	5	none	—	–30°	—	(66)	72
TfO	n-Bu	Mg	Br	5	NMP	—	–30°	—	(80)	73, 72
$(PhO)_2PO_2$	n-Bu	Mg	Cl	3	NMP	9	–20°	1.5	(90)	72
TfO	Ph	Mg	Br	5	NMP	—	–30°	—	(74)	73
$(PhO)_2PO_2$	n-C_8H_{17}	Mg	Cl	3	NMP	9	–20°	1.5	(90)	72
TfO	n-$C_{14}H_{29}$	Mg	Br	5	NMP	—	–30°	—	(67)	73

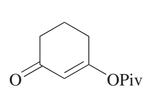
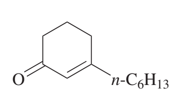
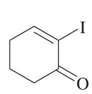
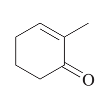
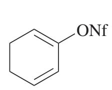
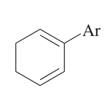
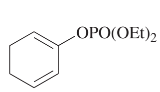
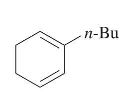
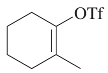
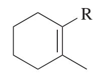
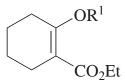
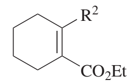
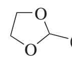
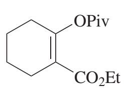
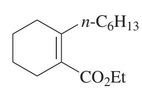
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	n-$C_6H_{13}MgCl$	$FeCl_2$ (1 mol %), Ligand **3** (2 mol %), THF, 0°, 10 min	 (65)	68
	MeMgCl	$Fe(acac)_3$ (1 mol %), NMP (9 eq), THF, 15–20°, 0.25 h	 (68)	54
	ArCu(CN)MgCl	$Fe(acac)_3$ (10 mol %), DMF, rt, 1 h	 Ar: 3-$CF_3C_6H_4$ (90) 4-$EtO_2CC_6H_4$ (86) 1-Np (72)	77
	n-BuMgCl	1. $Fe(acac)_3$ (1 mol %), THF, 20° 2. 20 min (slow add.) 3. 15 min	 (78)	58

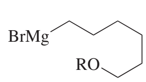
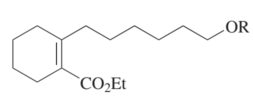
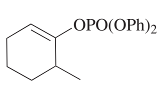
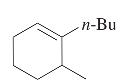
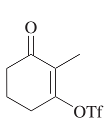
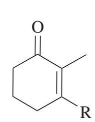
TABLE 1B. REACTION OF CYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

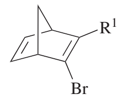
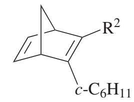
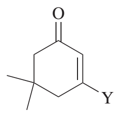
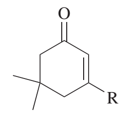
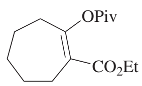
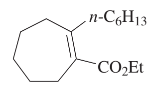
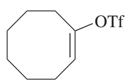
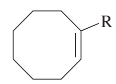
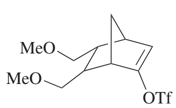
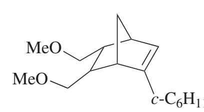
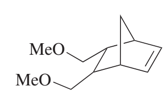
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	RMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, –30°	 R: *n*-Bu (53); 4-$MeOC_6H_4$ (62)	73
	R^2MgX	Catalyst (*x* mol %), additive (*y* eq), THF		

R^1	R^2	X	Catalyst	*x*	Additive	*y*	Temp (°)	Time (h)		Refs.
Piv	Me	Br	$FeCl_2$	1	LiCl	6	0	1	(<5)	68
Piv	Et	Br	$FeCl_2$	1	LiCl	6	0	1	(69)	68
Piv	*i*-Pr	Cl	$FeCl_2$	1	**3** (2 mol %)	—	0	1	(<5)	68
Tf	Ph	Br	$Fe(acac)_3$	10	NMP	—	–30	—	(53)	73
Piv	 $(CH_2)_5$	Br	$FeCl_2$	1	LiCl	6	0	1	(72)	68
Piv	$Ph(CH_2)_2$	Br	$FeCl_2$	1	LiCl	6	0	1	(51)	68
Piv	$Ph(CH_2)_3$	Br	$FeCl_2$	1	LiCl	6	0	1	(85)	68
Piv	$CH_2=CH(CH_2)_9$	Br	$FeCl_2$	1	LiCl	6	0	1	(90)	68
Piv	*n*-$C_{12}H_{25}$	Br	$FeCl_2$	1	LiCl	6	0	1	(81)	68
Tf	*n*-$C_{14}H_{29}$	Br	$Fe(acac)_3$	10	NMP	—	–30	—	(79)	76

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	*n*-C_6H_{13}MgX	Catalyst (1 mol %), additive (2 mol %), THF, 0°, 1 h		68

X	Catalyst	Additive	
Cl	$FeCl_2$	none	(79)
Cl	$FeCl_2$	PPh_3	(77)
Cl	$FeCl_2$	$P(c\text{-}C_6H_{11})_3$	(83)
Cl	$FeCl_2$	bpy	(75)
Cl	$FeCl_2$	TMEDA	(<5)
Cl	$FeCl_2$	**3**	(93)
Cl	$FeBr_2$	**3**	(86)
Cl	$FeCl_3$	**3**	(83)
Cl	$Fe(acac)_3$	**3**	(78)
Br	$FeCl_2$	**3**	(<5)
Br	$FeCl_2$	LiCl (6 eq)	(94)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_2$ (1 mol %), LiCl (6 eq), THF, 0°, 1 h	 R: Me (73); MOM (76); Bn (74); THP (74)	68
	*n*-BuMgBr	$Fe(acac)_3$ (6 mol %), NMP (9 eq), THF, –20°, 3 h	 (88)	72
	RMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, –30°	 R: Me (73); *n*-Bu (45); *n*-$C_{14}H_{29}$ (17)	73

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	c-C_6H_{11}MgCl (5 eq)	Fe(acac)$_3$ (20 mol %), DMPU, –25°, 0.75 h		180a
C_8				
	RMgBr	Catalyst (x mol %), NMP (y eq), THF		
	n-C_6H_{13}MgCl	FeCl$_2$ (1 mol %), LiCl (6 eq), THF, 0°, 1 h	 (78)	68
	RMgBr	Fe(acac)$_3$ (x mol %), THF/NMP, –30°		73
C_9				
	c-C_6H_{11}MgCl	Fe(acac)$_3$ (20 mol %), –25°, 0.75 h	 **I** +  **II**	180a

C$_7$ entry:

R^1	R^2		Refs.
H	H	(71)	180a
Br	c-C_6H_{11}	(75)	

C$_8$ entry (Y):

Y	R	Catalyst	x	y	Temp (°)	Time (h)		Refs.
Cl	n-Bu	Fe(acac)$_3$	1	9	–5 to 0	0.25	(79)	54
TfO	n-$C_{14}H_{29}$	**14**	5	—	–30	—	(67)	73

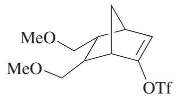
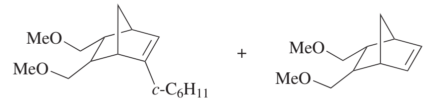
C$_8$ cyclooctenyl triflate entry:

R	x	
Ph	5	(61)
4-ClC$_6$H$_4$	5	(66)
n-$C_{14}H_{29}$	10	(60)

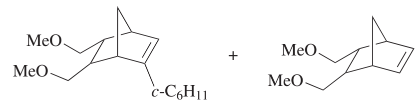
C$_9$ entry:

Solvent	**I**	**II**
Et$_2$O	(26)	(1)
THF	(81)	(6)
DME	(9)	(3)
NMP	(82)	(6)
DMPU	(88)	(1)
DMF	(50)	(5)
Et$_3$N	(5)	(4)
TMEDA	(0)	(0)
THF/NMP (1:3)	(88)	(6)
THF/NMP (1:1)	(79)	(5)
THF/NMP (3:1)	(78)	(12)
THF/DMPU (1:3)	(75)	(7)
THF/DMPU (1:1)	(66)	(8)
THF/DMPU (3:1)	(69)	(13)

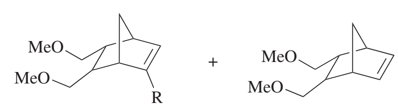
TABLE 1B. REACTION OF CYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	c-C_6H_{11}MgCl	Catalyst (20 mol %), –25°, 0.75 h	 **I** + **II**	180a

Catalyst	Solvent	I	II
$FeCl_3$	THF/NMP (1:3)	(79)	(8)
$FeCl_3$	DMPU	(85)	(4)
$Fe(dpm)_3$	THF/NMP (1:3)	(67)	(6)
$Fe(dpm)_3$	DMPU	(55)	(8)
$Fe(dbm)_3$	THF/NMP (1:3)	(72)	(6)
$Fe(dbm)_3$	DMPU	(68)	(7)
14	THF/NMP (1:3)	(63)	(4)
14	DMPU	(60)	(7)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	c-C_6H_{11}MgX (x eq)	$Fe(acac)_3$ (20 mol %), THF/NMP (1:3), 0.75 h	 **I** + **II**	180a

X	x	Temp (°)	I	II
Cl	5	–40	(78)	(6)
Cl	5	–25	(88)	(6)
Cl	5	0	(80)	(5)
Cl	5	25	(71)	(5)
Cl	5	50	(55)	(4)
Cl	10	–25	(61)	(11)
Cl	2.1	–25	(86)	(4)
Cl	1.1	–25	(93)	(1)
Br	5	–25	(80)	(8)
I	5	–25	(58)	(15)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgX (x mol %)	$Fe(acac)_3$ (20 mol %), –25°, 30–55 min	 **I** + **II**	180a

R	X	x	Solvent	I	II
Me	Br	5	THF/NMP (1:3)	(80)	(—)
c-C_3H_5	Br	1.6	DMPU	(67)	(3)
i-Pr	Cl	1.6	DMPU	(87)	(3)
c-C_4H_7	Cl	1.6	DMPU	(62)	(13)
s-Bu	Cl	1.6	DMPU	(87)	(—)
c-C_5H_9	Cl	1.6	DMPU	(71)	(7)
Ph	Cl	1.6	THF/NMP (1:3)	(85)	(—)
3-$MeOC_6H_4$	Br	1.6	THF/NMP (1:3)	(74)	(—)
3-$CF_3C_6H_4$	Br	1.6	THF/NMP (1:3)	(73)	(—)
c-C_7H_{13}	Cl	1.6	DMPU	(52)	(2)
Bn	Cl	2.1	THF/NMP (1:3)	(72)	(—)

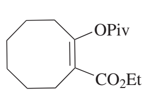
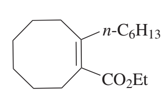
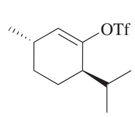
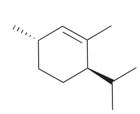
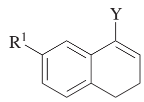
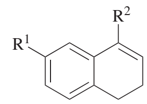
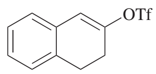
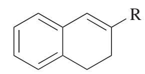
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	n-C_6H_{13}MgCl	$FeCl_2$ (1 mol %), ligand **3** (2 mol %), THF, 0°, 1 h	 (87)	68
C_{10} 	MeMgBr	$Fe(acac)_3$ (1.0 eq), THF/NMP, –30°	 (88)	73

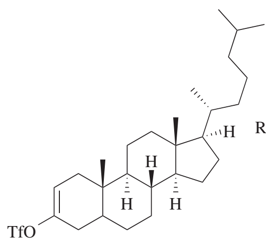
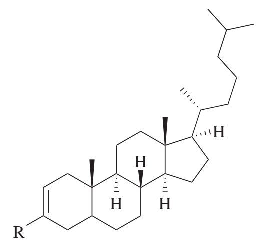
TABLE 1B. REACTION OF CYCLIC ALKENYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	R^2MgBr	$Fe(acac)_3$ (*x* mol %), NMP (*y* eq), THF		

R^1	Y	R^2	*x*	*y*	Temp (°)	Time (h)		Refs.
H	$(PhO)_2PO_2$	*n*-Bu	6	9	–20	3	(94)	72
MeO	TfO	*n*-$C_{14}H_{29}$	5	—	–30	—	(64)	73

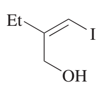
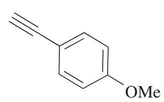
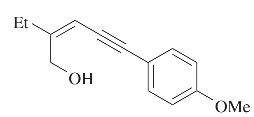
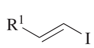
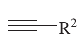
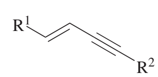
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, –30°		73

R	
Me	(89)
n-Bu	(88)
Ph	(66)

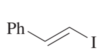
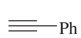
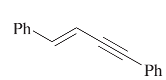
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{27}				
	RMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, –30°		73

R	
Me	(91)
Ph	(76)
$MOMO(CH_2)_8$	(91)
n-$C_{14}H_{29}$	(86)

TABLE 2. REACTION OF ALKENYL ELECTROPHILES WITH ALKYNES

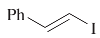
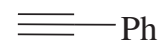
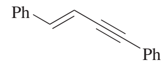
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		$FeCl_3$ (15 mol %), 1,10-phenanthroline (30 mol %), Cs_2CO_3 (3 eq), toluene, 110°, 48 h	 (25)[a]	64
$C_{6–8}$				
		$FeCl_3$ (15 mol %), 1,10-phenanthroline (30 mol %), Cs_2CO_3 (3 eq), toluene, 110°		64

R^1	R^2	Time (h)	
n-Bu	Ph	60	(70[a], 52)
n-Bu	4-$MeOC_6H_4$	60	(70[a], 61)
Ph	*n*-C_6H_{13}	36	(90[a], 85)
Ph	4-ClC_6H_4	48	(98[a], 90)
Ph	4-$MeOC_6H_4$	48	(83[a], 76)
4-$MeOC_6H_4$	4-ClC_6H_4	64	(70[a], 58)
4-$MeOC_6H_4$	4-$MeOC_6H_4$	48	(80[a], 69)

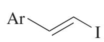
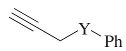
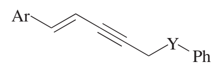
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		Catalyst (15 mol %), 1,10-phenanthroline (30 mol %), additive (3 eq), toluene, 110°	 (0)	64

Catalyst	Additive	Time (h)
$FeCl_3$	NaOH	24
$FeCl_3$	Na_2CO_3	24
$FeCl_3$	Et_3N	24
$FeCl_2$	Cs_2CO_3	24
$Fe(acac)_3$	Cs_2CO_3	48

TABLE 2. REACTION OF ALKENYL ELECTROPHILES WITH ALKYNES (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		$FeCl_3$ (*x* mol %), additive (*y* mol %), Cs_2CO_3 (3 eq), 110°		64

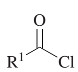
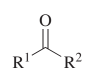
x	Additive	*y*	Solvent	Time (h)	
15	DMEDA	30	toluene	48	(25)[a]
15	TMEDA	30	toluene	48	(56)[a]
15	aniline	30	toluene	24	(0)
10	1,10-phenanthroline	10	toluene	48	(10)[a]
15	1,10-phenanthroline	15	toluene	48	(35)[a]
10	1,10-phenanthroline	20	toluene	48	(50)[a]
15	1,10-phenanthroline	30	toluene	48	(82[a], 69)
15	1,10-phenanthroline	30	DMF	48	(0)
15	L-proline	30	toluene	24	(0)
15	$HO_2C(CH_2)_2NMe_2$•HCl	30	toluene	24	(0)
15	pentane-2,4-dione	30	toluene	24	(0)
15	2-acetylcyclohexanone	30	toluene	24	(0)
15	*N*,*N′*-dimethylcyclohexane-1,2-diamine	30	toluene	24	(6)[a]

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (15 mol %), 1,10-phenanthroline (30 mol %), Cs_2CO_3 (3 eq), toluene, 110°		64

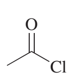
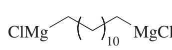
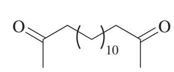
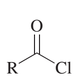
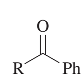
Ar	Y	Time (h)	
Ph	MeN	60	(80[a], 57)
Ph	O	60	(60[a], 45)
4-$MeOC_6H_4$	MeN	72	(67[a], 56)

[a] The yield was determined by NMR spectroscopy.

TABLE 3. REACTION OF ACYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

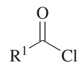
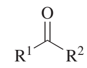
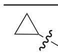
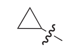
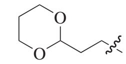
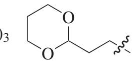
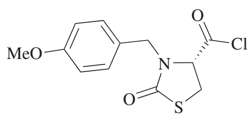
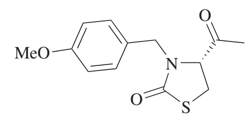
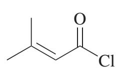
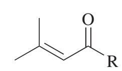
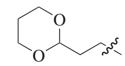
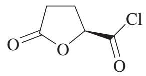
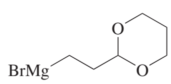
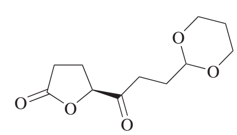
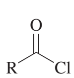
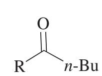
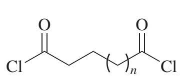
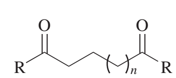
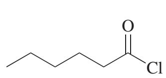
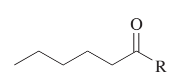
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{2–11}$				
	R^2MgX	$Fe(acac)_3$ (3 mol %), THF, rt		79

R^1	R^2	X	
Me	*n*-C_9H_{19}	Br	(82)
Me	*n*-$C_{10}H_{21}$	Br	(80)
n-Pr	*n*-Pr	Cl	(80)
n-Pr	*t*-Bu	Cl	(70)
n-Pr	Ph	Cl	(67)
i-Pr	*i*-Pr	Cl	(80)
i-Pr	Ph	Cl	(75)
n-C_5H_{11}	*n*-C_5H_{11}	Br	(82)
n-$C_{10}H_{21}$	Me	Cl	(84)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
		$Fe(acac)_3$ (6 mol %), THF, rt	 (80)	81
$C_{4–5}$				
	PhMgBr	$Fe(acac)_3$ (3 mol %), THF, 0°		79

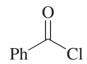
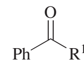
R	
n-Pr	(83)
i-Pr	(92)
t-Bu	(80)

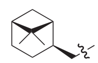
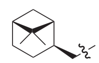
TABLE 3. REACTION OF ACYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

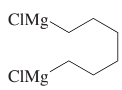
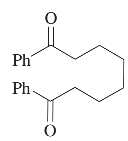
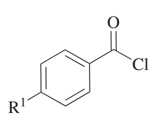
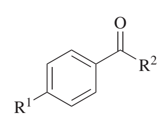
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{4-5} 	R^2MgBr	$Fe(acac)_3$ (3 mol %), THF, –78°	 R^1 | R^2  | n-C_6H_{13} (92)  |  (88) $MeO_2C(CH_2)_3$ | n-C_6H_{13} (95) $MeO_2C(CH_2)_3$ |  (76) $MeO_2C(CH_2)_3$ | $BnO(CH_2)_6$ (88) $MeO_2C(CH_2)_3$ | Ph (65) $MeO_2C(CH_2)_3$ | 4-$MeOC_6H_4$ (95)	73
C_4 	MeMgBr	$Fe(acac)_3$ (3 mol %), THF, –78°	 (80) er 99.5:0.5	73, 148
C_5 	RMgBr	$Fe(acac)_3$ (3 mol %), THF, –78°	 R n-C_6H_{13} (90)  (80)	73
		$Fe(acac)_3$ (3 mol %), THF, –78°	 (59) er 97:3	73
	n-BuMgX	$Fe(acac)_3$ (3 mol %), THF, rt	 R | X 2-furyl | Br (83[a], 75) 2-thienyl | Br (80)[a] $MeO_2C(CH_2)_3$ | Cl (78)[a]	80
C_{5-6} 	RMgCl	$Fe(acac)_3$ (3 mol %), THF, rt	 n | R 1 | Et (85[a], 76) — 80 2 | Et (90[a], 82) — 80 2 | n-C_6H_{13} (95) — 73	80, 80, 73
C_6 	RMgX	Catalyst (3 mol %), THF, rt		82

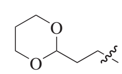
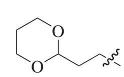
R	X	Catalyst	
Me	Cl	Fe(+3) resin	(84)[a]
Et	Br	Fe(+3) resin	(91)[a]
n-Bu	Cl	$Fe(acac)_3$	(97)
n-Bu	Cl	Fe(+3) resin	(98[a], 96)
n-Bu	Cl	Fe(+3) resin recycled	(94)[a]
Ph	Cl	Fe(+3) resin	(71)[a]
3-$MeOC_6H_4$	Cl	Fe(+3) resin	(63[a], 60)
n-C_9H_{19}	Br	Fe(+3) resin	(65[a], 61)

TABLE 3. REACTION OF ACYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	R^1MR^2	Catalyst (*x* mol %), additive, THF		

R^1	M	R^2	Catalyst	*x*	Additive	Temp	Time (h)		Refs.
Me	Mg	Cl	$Fe(acac)_3$	3	none	rt	—	(80)	79
Me	Mg	Cl	Fe(+3) resin	3	none	rt	—	(86)[a]	82
Et	Mg	Br	Fe(+3) resin	3	none	rt	—	(67)[a]	82
i-Pr	Mg	Cl	$Fe(acac)_3$	3	none	rt	—	(84)	79
n-Bu	Mg	Br	$Fe(acac)_3$	3	none	rt	—	(90)	79
n-Bu	Mg	Br	Fe(+3) resin	3	none	rt	—	(57)[a]	82
t-Bu	Mg	Cl	$Fe(acac)_3$	3	none	rt	—	(70)	79
Ph	Mg	Cl	$Fe(acac)_3$	3	none	0°	—	(75)	79
Ph	Mg	Cl	$Fe(acac)_3$	3	none	rt	—	(63)	79
Ph	Mg	Cl	Fe(+3) resin	3	none	rt	—	(79)[a]	82
$3\text{-}MeOC_6H_4$	Mg	Cl	Fe(+3) resin	3	none	rt	—	(52)[a]	82
$t\text{-}BuO_2C(CH_2)_5$	Zn	$t\text{-}BuO_2C(CH_2)_5$	$FeCl_3$	10	NMP	–10°	1	(82)	84
$n\text{-}C_9H_{19}$	Mg	Br	Fe(+3) resin	3	none	rt	—	(42)[a]	82
	Zn		$FeCl_3$	10	NMP	–10°	1	(80)	84

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (6 mol %), THF, rt	 (65)	81
$C_{7–8}$ 	R^2MgX	$Fe(acac)_3$ (3 mol %), THF		

R^1	R^2	X	Temp		Refs.
Cl	Me	Cl	rt	(85[a], 78)	80
Cl	Me	Br	–78°	(81)	73
Cl	Et	Br	–78°	(87)	73
Cl	$n\text{-}C_6H_{13}$	Br	–78°	(97)	73
Cl	Ph	Br	rt	(82)[a]	80
Cl	$4\text{-}MeOC_6H_4(CH_2)_2$	Br	–78°	(96)	73
Cl		Br	–78°	(83)	73
Br	Me	Br	–78°	(86)	73
Br	Et	Br	–78°	(89)	73
Br		Br	–78°	(69)	73
Br	$n\text{-}C_6H_{13}$	Br	–78°	(84)	73
Br	$4\text{-}MeOC_6H_4(CH_2)_2$	Br	–78°	(90)	73
MeO	$n\text{-}C_6H_{13}$	Br	–78°	(99)	73
MeO	Ph	Cl	rt	(80)[a]	80
NC	Me	Cl	rt	(75)[a]	80

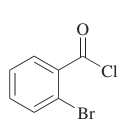
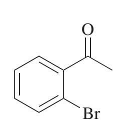
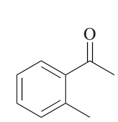
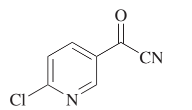
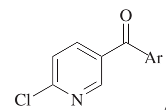
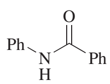
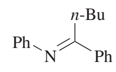
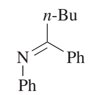
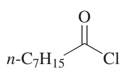
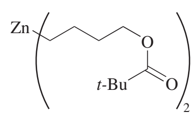
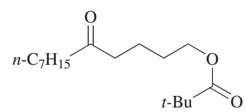
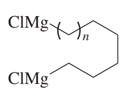
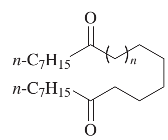
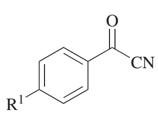
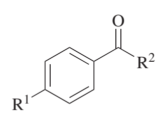
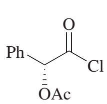
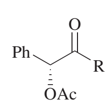
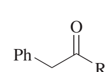
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	MeMgBr	$Fe(acac)_3$ (3 mol %), THF, –78°	 (85) +  (7)	73

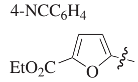
TABLE 3. REACTION OF ACYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	ArMgX	$Fe(acac)_3$ (5 mol %), THF, 25 min		83
	n-BuMgCl	1. $SOCl_2$, 80°, 1 h 2. n-BuMgCl, $Fe(acac)_3$ (5 mol %), THF/NMP, 0°, 5 min	 I +  II **I** + **II** (72), **I**/**II** = 7:1	146
C_8				
		$FeCl_3$ (10 mol %), THF/NMP, –10°, 1 h	 (74)	84
		$Fe(acac)_3$ (6 mol %), THF, rt		81

Ar	X	Temp (°)	
Ph	Cl	0	(79)
$4-MeOC_6H_4$	Br	0	(86)
$4-EtO_2CC_6H_4$	Cl	–10	(75)

n	
1	(72)
5	(70)
7	(71)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-9}				
	R^2MgX	$Fe(acac)_3$ (5 mol %), THF, 25 min		83
C_8				
	RMgBr	$Fe(acac)_3$ (3 mol %), THF, –78°	 I +  II	73

R^1	R^2	X	Temp (°)	
MeO	$4-MeOC_6H_4$	Br	0	(98)
MeO	$4-NCC_6H_4$	Cl	–10	(84)
MeO		Cl	–10	(78)
H	Ph	Cl	0	(84)
H	$4-NCC_6H_4$	Cl	–10	(78)
H	$4-EtO_2CC_6H_4$	Cl	–10	(80)
Cl	$4-NCC_6H_4$	Cl	0	(89)
Cl	$4-EtO_2CC_6H_4$	Cl	–10	(74)
EtO_2C	$4-MeOC_6H_4$	Br	–10	(83)
EtO_2C	$4-NCC_6H_4$	Cl	–10	(71)
EtO_2C	$2-EtO_2CC_6H_4$	Cl	–10	(66)
EtO_2C	$4-EtO_2CC_6H_4$	Cl	–10	(68)

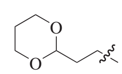
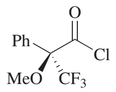
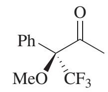
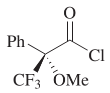
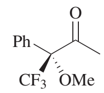
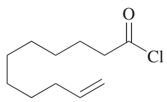
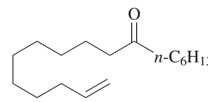
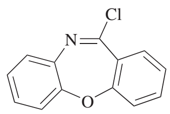
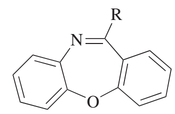
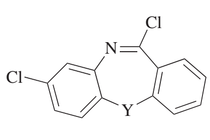
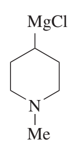
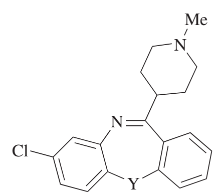
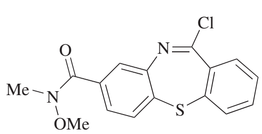
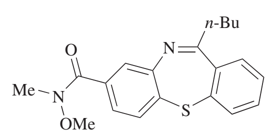
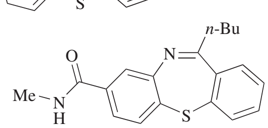
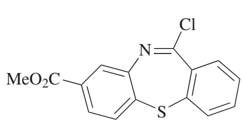
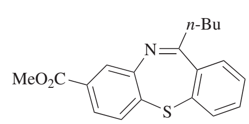
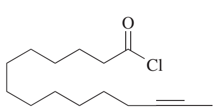
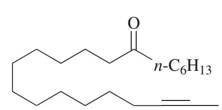
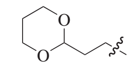
R	I	I er	II
$n-C_6H_{13}$	(43)	>99.5:0.5	(5)
	(78)	>99.5:0.5	(—)

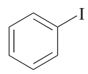
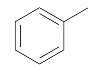
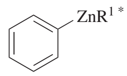
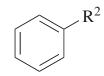
TABLE 3. REACTION OF ACYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	MeMgCl	$Fe(acac)_3$ (3 mol %), THF, rt	 (95^a, 90)	80
	MeMgCl	$Fe(acac)_3$ (3 mol %), THF, rt	 (85^a, 76)	80
C_{11}				
	$n\text{-}C_6H_{13}MgBr$	$Fe(acac)_3$ (3 mol %), THF, –78°	 (95)	73
C_{13}				
	RMgBr	Catalyst (5 mol %), additive, THF		146
		$Fe(acac)_3$ (5 mol%), THF/NMP, rt, 5 min	 Y: HN (82); O (71); S (86)	146
C_{14}				
	n-BuMgCl	$Fe(acac)_3$ (5 mol %), THF/NMP, –78°, 5 min	 (70) +  (<5)	146
	n-BuMgCl	$Fe(acac)_3$ (5 mol %), THF/NMP, –78°, 5 min	 (89)	146
C_{15}				
	$n\text{-}C_6H_{13}MgBr$	$Fe(acac)_3$ (3 mol %), THF, –78°	 (79)	73

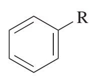
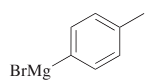
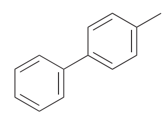
R	Catalyst	Additive	Temp	Time (min)	
Me	$Fe(acac)_3$	NMP	rt	5	(17)
$TMSCH_2$	$Fe(acac)_3$	NMP	rt	5	(72)
n-Bu	$Fe(acac)_3$	none	rt	5	(22)
n-Bu	$Fe(acac)_3$	NMP	rt	5	(96)
n-Bu	$Fe(acac)_3$	NMP	–78°	5	(94)
n-Bu	$FeCl_3$	NMP	rt	5	(96)
t-Bu	$Fe(acac)_3$	NMP	rt	5	(27)
$c\text{-}C_6H_{13}$	$Fe(acac)_3$	NMP	rt	5	(93)
Ph	$Fe(acac)_3$	NMP	rt	30	(55)
	$Fe(acac)_3$	NMP	rt	5	(95)

[a] The yield was determined by GLC.

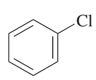
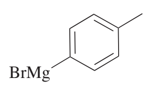
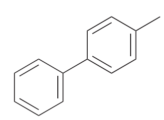
TABLE 4. REACTION OF ARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	Me_3FeLi (5 eq)	Et_2O, –78°, 3 h	 (50)	106
	$Zn(R^2)_2$	$Fe(acac)_3$ (10 mol %), $BrCH_2CH_2Br$ (1 eq), THF, rt, 3 h		141

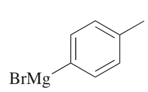
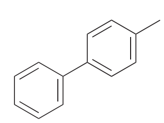
R^1	R^2	
Me	*i*-Pr	(79)[a]
i-Pr	*i*-Pr	(58)
Ph	*i*-Pr	(96)
Me	*s*-Bu	(76)[a]
Me	*t*-Bu	(5)
Me	*n*-C_8H_{17}	(72)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Catalyst (3 mol %), SIPr•HCl (9 mol %), THF, additive (*x* mol %), 0° 2. rt, 4 h 3. 60°, 24 h		

R	Catalyst	Additive	*x*		Refs.
F	FeF_3•$3H_2O$	EtMgBr	18	(0)	93, 94
Cl	FeF_3	none	—	(72)	94
Cl	FeF_3	MeMgBr	18	(97)	94
Cl	FeF_3	MeMgBr	27	(97)	94
Cl	FeF_3	EtMgBr	9	(98)	93
Cl	FeF_3	EtMgBr	18	(96)	93
Cl	FeF_3•$3H_2O$	EtMgBr	18	(98)	93, 94
Cl	FeF_3•$3H_2O$	EtMgBr	27	(97)	93, 94
Br	FeF_3•$3H_2O$	EtMgBr	18	(28)	93, 94
I	FeF_3•$3H_2O$	EtMgBr	18	(23)	93, 94
TfO	FeF_3•$3H_2O$	EtMgBr	18	(27)	93

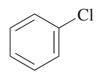
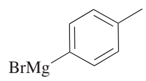
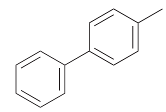
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (5 mol %), additive 1 (*x* mol %), additive 2 (*y* mol %), THF, 60°, 24 h		

Catalyst	Additive 1	*x*	Additive 2	*y*		Refs.
FeF_2	SIPr•HCl	15	none	—	(18)	93, 94
FeF_2•$4H_2O$	SIPr•HCl	15	none	—	(96)	93, 94
FeF_3	SIPr•HCl	15	none	—	(29)	93, 94
FeF_3	SIPr•HCl	15	H_2O	15	(40)	93, 94
$FeCl_3$	none	—	none	—	(17)	93, 94
$FeCl_3$	SIPr•HCl	15	none	—	(32)	93, 94
$FeCl_3$	SIPr•HCl	15	KF	20	(92)	93, 94
$FeCl_3$	SIPr•HCl	15	TBAF	20	(65)	93
$Fe(acac)_3$	SIPr•HCl	15	none	—	(26)	93, 94

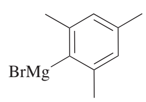
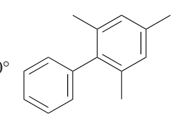
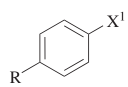
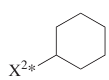
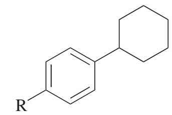
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		FeF_3•$3H_2O$ (5 mol %), additive (*x* mol %), THF, 60°, 24 h		

Additive	*x*		Refs.
none	—	(6)	93, 94
IPr•HCl	15	(25)	93, 94
SIPr•HCl	5	(61)	93, 94
SIPr•HCl	10	(93)	93, 94
SIPr•HCl	15	(98)	93, 94
SIPr•HBF_4	15	(39)	93, 94
3	15	(34)	93, 94
I-*t*-Bu•HCl	15	(51)	93, 94
I-Adm•HBF_4	15	(8)	93

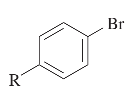
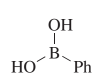
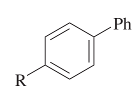
TABLE 4. REACTION OF ARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
 *Continued from previous page.*		FeF_3•$3H_2O$ (5 mol %), additive (*x* mol %), THF, 60°, 24 h		

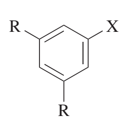
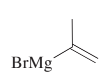
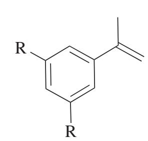
Additive	*x*		Refs.
I-MeBu•HBF_4	15	(2)	93
PPh_3	10	(2)	93
P(*c*-C_6H_{11})$_3$	10	(5)	93, 94
(*c*-C_6H_{11})$_2$P(MeO-biphenyl)	10	(2)	93
(*t*-Bu)$_2$P(biphenyl)	10	(2)	93
DPPE	10	(0)	93, 94
DPPF	10	(1)	93, 94
phenanthroline	5	(1)	93, 94
TMEDA	250	(1)	93, 94

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. FeF_3•$3H_2O$ (3 mol %), SIPr•HCl (9 mol %), EtMgBr (18 mol %), THF, 0° 2. rt, 4 h 3.Toluene, 120°, 24 h	 (93)	93, 94
C_{6-7}				
		$FeCl_3$ (5 mol %), TMEDA (1.2 eq), Mg (1.2 eq), THF, 0°, 3 h		145

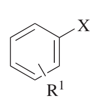
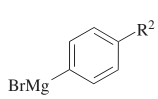
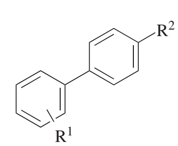
R	X^1	X^2	
H	Cl	Br	(20)
H	Br	Cl	(25)
H	Br	Br	(77)
F	Br	Br	(48)
MeO	Br	Br	(65)
CF_3	Br	Br	(68)[b]
Me_2N	Br	Br	(72)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (5 mol %), dppy (10 mol %), KF/KOH (1:1), THF, 100°, 48 h		98

R	Pressure (bar)	
H	15,000	(97)
Me	15,000	(67)
Me	1	(<1)

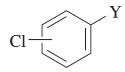
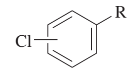
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		1. $FeCl_3$ (10 mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0.5 h		47

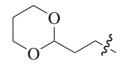
R	X	
H	I	(—)
MeO	Br	(—)

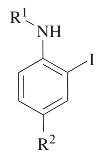
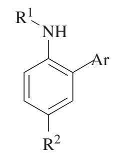
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-10}				
		1. FeF_3•$3H_2O$ (*x* mol %), SIPr•HCl (*y* mol %), EtMgBr (*z* mol %), THF, 0° 2. rt, 4 h 3. Temp, time		

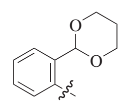
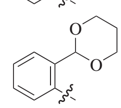
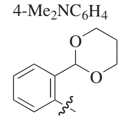
R^1	X	R^2	*x*	*y*	*z*	Temp (°)	Time (h)		Refs.
4-MeO	Cl	Me	3	9	18	60	24	(92)	93, 94
4-F	Cl	MeO	3	9	18	60	24	(91)	93, 94
3,4-F_2	Cl	MeO	5	15	30	60; then 80	24; 12	(81)	93, 94
3,5-F_2	Br	MeO	5	15	30	40	36	(12)	93, 94
4-*n*-Bu	Cl	F	3	9	18	60	24	(87)	93, 94
2-CH_2=CH(CH_2)$_2$	Br	Me	5	15	30	60	80	(18)	94

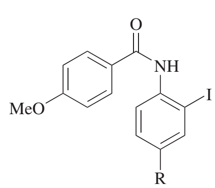
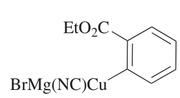
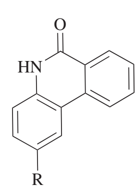
TABLE 4. REACTION OF ARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	RMgBr	Catalyst (*x* mol %), additive (*y* mol %), THF		

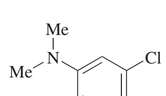
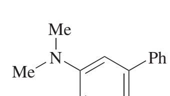
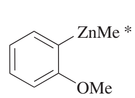
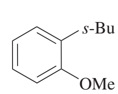
Isomer	Y	R	Catalyst	*x*	Additive	*y*	Temp (°)	Time (h)		Refs.
2-	Cl	*n*-C_8H_{17}	Fe(acac)$_3$	10	NMP	—	–78 to –40	1	(39)	73
3-	Cl	*n*-C_8H_{17}	Fe(acac)$_3$	10	NMP	—	–78 to –40	1	(77)	73
4-	Cl		Fe(acac)$_3$	5	none	—	–78	3	(0)	73
4-	Br	4-MeOC$_6$H$_4$	FeF$_3$•3H$_2$O	6	SIPr•HCl	18	60	24	(4)	94
4-	Cl	*n*-C_8H_{17}	Fe(acac)$_3$	10	NMP	—	–78 to –40	1	(58)	73
4-	TfO	*n*-C_8H_{17}	Fe(acac)$_3$	10	NMP	—	–78	1	(76)	73

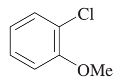
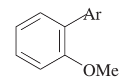
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-7}				
	ArCu(CN)MgX	Fe(acac)$_3$ (10 mol %), DME, THF, 80°		97

R^1	R^2	Ar	X	Time (h)	
Ac	H	4-MeOC$_6$H$_4$	Br	4	(74)
CF$_3$CO	H	4-MeOC$_6$H$_4$	Br	5	(55)
Tf	H	4-MeOC$_6$H$_4$	Br	5	(68)
Ts	H	4-MeOC$_6$H$_4$	Br	5	(84)
Bz	H	4-MeOC$_6$H$_4$	Br	4	(85)
4-MeOC$_6$H$_4$CO	H	4-MeOC$_6$H$_4$	Br	7	(92)
4-MeOC$_6$H$_4$CO	TIPSO	4-NCC$_6$H$_4$	Cl	2	(96)
4-MeOC$_6$H$_4$CO	MeO	3,4-OCH$_2$OC$_6$H$_3$	Br	3	(84)
4-MeOC$_6$H$_4$CO	MeO	4-NCC$_6$H$_4$	Br	4	(74)
4-MeOC$_6$H$_4$CO	CF$_3$	3-NCC$_6$H$_4$	Br	3	(70)
4-MeOC$_6$H$_4$CO	TIPSO		Br	3	(82)
4-MeOC$_6$H$_4$CO	EtO$_2$C		Br	4	(75)
4-MeOC$_6$H$_4$CO	NC	4-Me$_2$NC$_6$H$_4$	Br	3	(71)
4-MeOC$_6$H$_4$CO	NC		Br	3	(70)

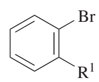
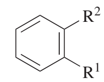
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Fe(acac)$_3$ (10 mol %), DME, THF, 80°		97

R	Time (h)	
MeO	2	(92)
CF$_3$	3	(78)

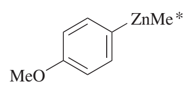
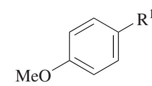
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	PhMgBr	1. FeF$_3$•3H$_2$O (3 mol %), SIPr•HCl (9 mol %), EtMgBr (18 mol %), THF, 0° 2. rt, 4 h 3. 60°, 24 h	 (94)	93, 94
 *	(*s*-Bu)$_2$Zn	Fe(acac)$_3$ (10 mol %), BrCH$_2$CH$_2$Br (1 eq), THF, rt, 3 h	 (22)[a]	141

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	ArMgBr	1. FeF_3•$3H_2O$ (*x* mol %), SIPr•HCl (*y* mol %), EtMgBr (*z* mol %), THF, 0° 2. rt, 4 h 3. Temp, time		

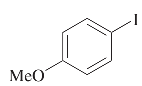
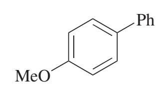
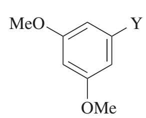
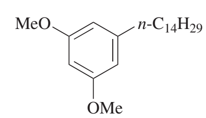
Ar	*x*	*y*	*z*	Temp (°)	Time (h)		Refs.
2-MeC_6H_4	3	9	18	80	24	(90)	94
1-Np	5	15	30	70	48	(92)	93, 94
2-Np	3	9	18	70	48	(96)	93, 94

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{6–7}$ 	R^2X*	$FeCl_3$ (5 mol %), TMEDA (1.2 eq), Mg (1.2 eq), THF, 0°, 3 h		145

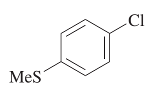
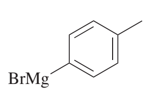
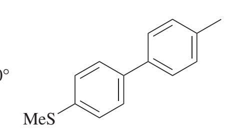
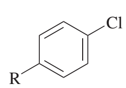
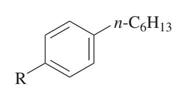
R^1	R^2	X	
MeO	*c*-C_6H_{11}	Cl	(63)
MeO	*c*-C_6H_{11}	Br	(66)
MeO	$Ph(CH_2)_3$	Br	(74)[a]
EtO_2C	*n*-$C_{12}H_{25}$	Br	(51)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	R^1ZnR^2	$Fe(acac)_3$ (10 mol %), $BrCH_2CH_2Br$ (1 eq), THF, rt		141

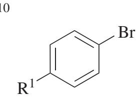
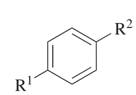
R^1	R^2	Time (h)	
allyl	allyl	3	(8)[a]
n-Pr	*n*-Pr	3	(69)
i-Pr	*i*-Pr	3	(67)
s-Bu	*s*-Bu	3	(68)
3-pentyl	3-pentyl	3	(34)
$EtO_2C(CH_2)_3$	Me	6	(66)
c-C_6H_{11}	*c*-C_6H_{11}	3	(71)
Bn	Bn	3	(6)
2-octyl	2-octyl	3	(68)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhCu(CN)MgCl	$Fe(acac)_3$ (10 mol %), DME, THF, 80°, 12 h	 (—)	96
	*n*-$C_{14}H_{29}MgBr$	$Fe(acac)_3$ (5 mol %), THF, Et_2O, NMP, rt, 5 min		

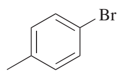
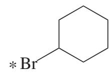
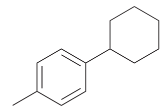
Y		Refs.
Cl	(0)	85, 43
TsO	(0)	85
TfO	(90)	85, 43

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. FeF_3•$3H_2O$ (6 mol %), SIPr•HCl (18 mol %), EtMgBr (36 mol %), THF, 0° 2. rt, 4 h 3. 60°, 24 h	 (80)	93, 94
	*n*-$C_6H_{13}MgBr$	$Fe(acac)_3$ (5 mol %), THF, Et_2O, NMP, rt, 5 min		85, 43

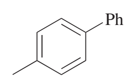
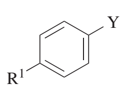
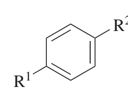
R	
i-$PrSO_3$	(94)
(*i*-Pr)$_2NO_2S$	(94)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{7–10}$ 	R^2X*	$FeCl_3$ (5 mol %), TMEDA (1.2 eq), Mg (1.2 eq), THF		145

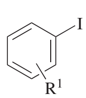
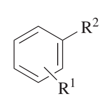
R^1	R^2	X	Temp (°)	Time (h)	
Me	*s*-Bu	Br	0	3	(62)
Me	$CH_2{=}CH(CH_2)_3$	Br	0	3	(50)
Me	*t*-$BuO_2C(CH_2)_4$	Br	0	3	(38)
Me	*c*-C_6H_{11}	Cl	0–20	4	(75)
Me	*n*-$C_{12}H_{25}$	Br	0	3	(80)
t-Bu	*i*-$PrCH_2$	Br	0	3	(67)
t-Bu	*n*-$C_{12}H_{25}$	Br	0	3	(81)

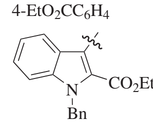
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$FeCl_3$ (*x* mol %), additive (1.2 eq), Mg (1.2 eq)		145

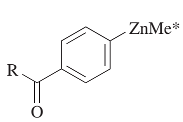
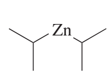
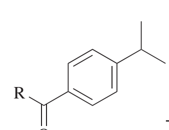
x	Additive	Solvent	Temp (°)	Time (h)	
5	none	THF	0	1	(27)
5	TMEDA	THF	0	2	(69)
5	TMEDA	THF	0	3	(70)
5	TMEDA	THF	20	2	(62)
5	TMEDA	THF	45	2	(53)
7.5	TMEDA	THF	0	2	(72)
10	TMEDA	THF	0	2	(75)
5	TMEDA	Et_2O	20	2	(0)
5	TMEDA	*t*-BuOMe	20	2	(0)
5	TMEDA	1,4-dioxane	20	2	(10)
5	TMEDA	cyclohexane	20	2	(0)
5	TMEDA	2-MeTHF	20	2	(65)
5	pyridine	THF	0	1	(0)
5	1,10-phenanthroline	THF	0	1	(0)
5	$PhNMe_2$	THF	0	1	(31)
5	Et_3N	THF	0	1	(32)
5	*trans-N,N,N′,N′*-tetramethyl-1,2-diaminocyclohexane	THF	0	1	(38)
5	*trans*-1,2-diaminocyclohexane	THF	0	1	(0)
5	NMP	THF	0	1	(<5)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$Cp(PMe_2Ph)_2FeBr$ (5 mol %), Et_2O, 24 h	 (0)	95
	R^2MgBr	$Fe(acac)_3$ (5 mol %), THF, Et_2O, NMP, rt, 5 min		

R^1	Y	R^2		Refs.
Me	Cl	*n*-$C_{14}H_{29}$	(0)	85, 43
Me	TfO	*n*-$C_{14}H_{29}$	(81)	85, 43
Me	TsO	*n*-$C_{14}H_{29}$	(0)	85, 43
CF_3	Cl	*n*-$C_{14}H_{29}$	(94)	85, 43
CF_3	TfO	*n*-$C_{14}H_{29}$	(72)	85, 43
CF_3	TsO	*n*-$C_{14}H_{29}$	(75)	85, 43
NC	Cl	*n*-C_6H_{13}	(91)	85, 43, 87
NC	TfO	*n*-C_6H_{13}	(80)	85, 43, 87
NC	TsO	*n*-C_6H_{13}	(80)	85, 43

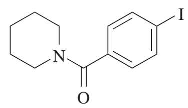
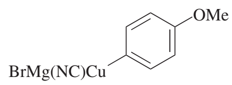
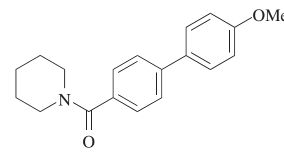
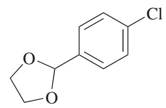
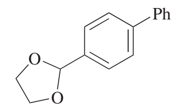
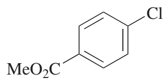
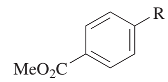
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	$R^2Cu(CN)MgCl$	$Fe(acac)_3$ (10 mol %), DME, THF, 80°		96

R^1	R^2	Time (h)	
2-EtO_2C	Ph	2	(58)
2-EtO_2C	4-$TfOC_6H_4$	2	(62)
3-EtO_2C	Ph	2	(82)
4-EtO_2C	Ph	10	(70)
4-NC	4-$EtO_2CC_6H_4$	3	(72)
4-NC		6	(85)

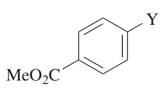
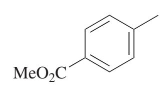
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (10 mol %), $BrCH_2CH_2Br$ (1 eq), THF, rt		141

R	Time (h)	
MeO	3	(74)
1-piperidyl	6	(68)

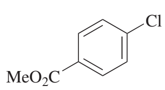
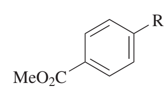
TABLE 4. REACTION OF ARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$Fe(acac)_3$ (10 mol %), DME, THF, rt, 2 h	 (58)	96
	PhMgBr	1. FeF_3•$3H_2O$ (3 mol %), SIPr•HCl (9 mol %), EtMgBr (18 mol %), THF, 0° 2. rt, 4 h 3. 60°, 24 h; then 80°, 12 h	 (88)	93, 94
	See table.	$Fe(acac)_3$ (5 mol %), NMP, THF, 5 min		

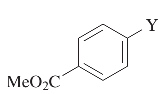
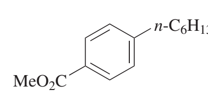
Nucleophile	Cosolvent	Temp	R		Refs.
$Et_3ZnMgBr$	Et_2O	rt	Et	(93)	85, 43
n-BuLi	Et_2O	rt	*n*-Bu	(0)	85
n-$C_{14}H_{29}MnCl$	none	0°	*n*-$C_{14}H_{29}$	(96)	43
(*n*-$C_{14}H_{29})_2Mn$	none	0°	*n*-$C_{14}H_{29}$	(>98)	43
(*n*-$C_{14}H_{29})_3MnMgCl$	none	0°	*n*-$C_{14}H_{29}$	(>98)	43

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[(Me_4Fe)(MeLi)][Li(OEt_2)]_2$	THF, –30°		

Y		Refs.
Cl	(<20)	107, 41
I	(<20)	107, 41
TfO	(<20)	107

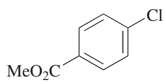
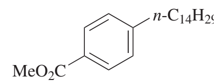
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgBr	Catalyst (5 mol %), NMP, THF		

R	Catalyst	Cosolvent	Temp	Time (min)		Refs.
CH_2=CH	$FeCl_2$	Et_2O	rt	5	(0)	85
Et	$FeCl_2$	Et_2O	rt	5	(95)	85, 43
CH=$CHCH_2$	$FeCl_2$	Et_2O	rt	5	(0)	85
i-Pr	$Fe(acac)_3$	Et_2O	rt	5	(59)	85, 43
n-C_6H_{13}	$FeCl_2$	Et_2O	rt	5	(>95)	85
n-C_6H_{13}	$Fe(acac)_3$	Et_2O	rt	5	(>95[a], 91)	85, 43
CH_2=$CH(CH_2)_4$	$FeCl_2$	Et_2O	rt	5	(91)	85, 43
Ph	$FeCl_2$	Et_2O	rt	5	(28)	85, 43
$MOMO(CH_2)_8$	$FeCl_2$	Et_2O	rt	5	(88)	85, 43
n-C_9H_{19}	$FeCl_2$	none	0° to rt	7	(79–84)	87, 41
$—\equiv—(CH_2)_8$	$Fe(acac)_3$	Et_2O	rt	5	(85)	85, 43

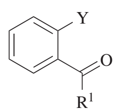
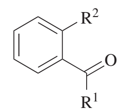
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	*n*-$C_6H_{13}MgBr$	$Fe(acac)_3$ (5 mol %), NMP, THF, Et_2O, rt, 5 min		

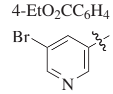
Y		Refs.
Br	(38)	85
I	(27)	85
TfO	(>95[a], 87)	85, 43
TsO	(>95[a], 83)	85, 43

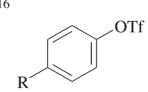
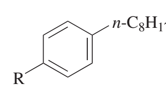
TABLE 4. REACTION OF ARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	n-$C_{14}H_{29}MgBr$	Catalyst (5 mol %), additive, 5 min		

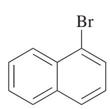
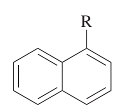
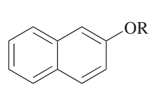
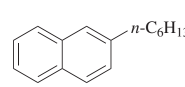
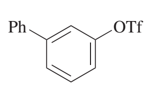
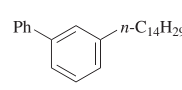
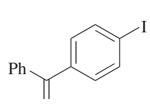
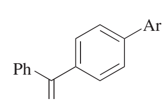
Catalyst	Additive	Solvent	Temp	Yield	Refs.
$FeCl_3$	none	THF	rt	(>95)	43
$FeCl_3$	none	THF	–60°	(>95)	43
$FeCl_2$	none	THF	rt	(>95)	43
$FeCl_2$	none	THF	–60°	(>95)	43
$Fe(acac)_3$	NMP	THF/Et_2O	rt	(91)	85

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{8–13}$ 	$R^2Cu(CN)MX$	$Fe(acac)_3$ (10 mol %), DME, THF, rt		96

Y	R^1	R^2	MX	Time (h)	Yield
I	Me	Ph	MgCl	1	(86)
I	n-Bu	4-$MeO_2CC_6H_4$	MgCl	4	(68)
Cl	Ph	Ph	MgCl	18	(—)
Br	Ph	Ph	MgCl	18	(—)
I	Ph	Ph	Li	0.5	(90)
I	Ph	Ph	MgCl	0.5	(93)
TsO	Ph	Ph	MgCl	0.5	(—)
TfO	Ph	Ph	MgCl	2	(—)
I	Ph	4-$MeOC_6H_4$	MgBr	2	(76)
I	Ph	2-$EtO_2CC_6H_4$	MgCl	12	(75)
I	Ph	4-$EtO_2CC_6H_4$	MgCl	2	(86)
I	n-Bu		MgCl	22	(57)

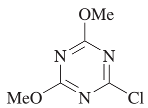
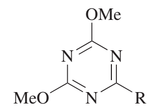
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{8–16}$ 	n-$C_8H_{17}MgBr$	$Fe(acac)_3$ (15 mol %), NMP (8 eq), THF, rt		

R	Time (h)	Yield	Refs.
$AcO(CH_2)_2$	1	(84)	149
4-$MeC_6H_4(CH_2)_3$	0.5	(90)	49

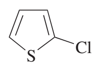
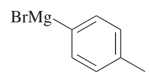
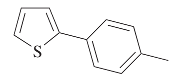
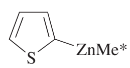
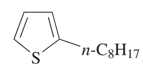
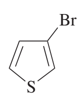
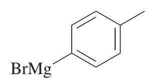
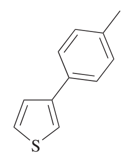
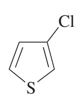
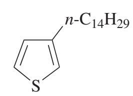
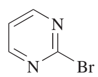
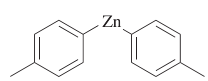
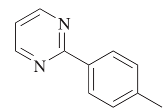
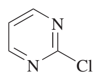
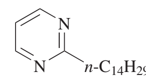
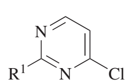
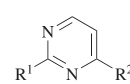
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	RBr*	$FeCl_3$ (5 mol %), TMEDA (1.2 eq), Mg (1.2 eq), THF, 0°, 3 h	 R: c-C_6H_{11} (67); n-$C_{12}H_{25}$ (75)	145
	n-$C_6H_{13}MgCl$	$FeCl_2$ (1 mol %), Ligand **3** (2 mol %), THF, 0°, 1 h	 R: Piv (40); Me_2NCO (80)	68
C_{12} 	n-$C_{14}H_{29}MgBr$	$Fe(acac)_3$ (5 mol %), THF, NMP, 0°, 5 min	 (81)	43
C_{13} 	ArCu(CN)MgCl	$Fe(acac)_3$ (10 mol %), DME, THF, rt, 4 h	 Ar: Ph (80); 4-$EtO_2CC_6H_4$ (50)	96

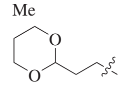
[a] The yield was determined by GLC.
[b] The yield was determined by NMR spectroscopy.

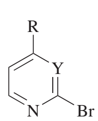
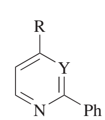
TABLE 5. REACTION OF HETEROARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	RMgBr	$Fe(acac)_3$ (5 mol %), additive, THF		

R	Additive	Temp (°)	Time (min)		Refs.
Ph	none	–30	10	(63)	43, 87
n-$C_{14}H_{29}$	NMP	0	5	(84)	43

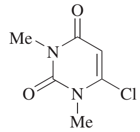
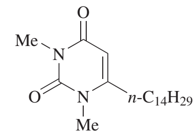
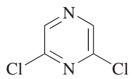
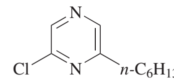
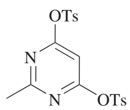
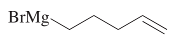
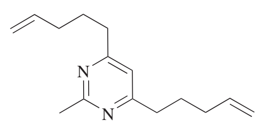
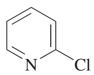
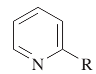
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		1. FeF_3 (4 mol %), SIPr•HCl (12 mol %), EtMgBr (12 mol %), THF, 0° 2. rt, 4 h 3. 50°, 15 h	 (4)	94
	$(n\text{-}C_8H_{17})_2Zn$	$Fe(acac)_3$ (10 mol %), $BrCH_2CH_2Br$ (1 eq), THF, rt, 3 h	 (72)	141
		1. FeF_3 (2 mol %), SIPr•HCl (6 mol %), EtMgBr (6 mol %), THF, 0° 2. rt, 4 h 3. 60°, 18 h	 (3)	94
	n-$C_{14}H_{29}MgBr$	$Fe(acac)_3$ (5 mol %), THF, Et_2O, NMP, rt, 5 min	 (41)	94
		$FeCl_2(dppbz)_2$ (5 mol %), THF, toluene, 100°, 4 h	 (58)	99
	n-$C_{14}H_{29}Br$	$Fe(acac)_3$ (5 mol %), NMP, THF, Et_2O, rt, 5 min	 (93)	85, 43
	R^2MgBr	$Fe(acac)_3$ (5 mol %), additive, THF		

R^1	R^2	Additive	Temp (°)	Time (min)		Refs.
Cl	Me	none	–78	180	(51)	73
Cl		none	–78	180	(70)	73
Cl	n-C_6H_{13}	none	–78	180	(83)	73
Cl	4-$MeOC_6H_4$	none	–78	180	(71)	73
MeS	Ph	none	–30	10	(53)	43
MeS	n-$C_{14}H_{29}$	NMP	0	5	(89)	43, 87

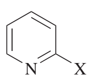
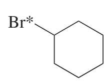
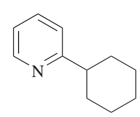
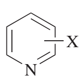
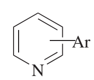
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{4–6}$				
	$Na[BPh_4]$	$FeCl_2(dppbz)_2$ (5 mol %), $(4\text{-}MeOC_6H_4)_2Zn$ (10 mol %), THF, toluene, reflux, 16 h		99

R	Y	
H	N	(69[a], 51)
H	CH	(76[a], 64)
MeO_2C	CH	(94[a], 52)

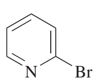
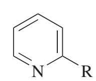
TABLE 5. REACTION OF HETEROARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	n-$C_{14}H_{29}MgBr$	$Fe(acac)_3$ (5 mol %), THF, NMP, 0°, 5 min	 (60)	43
	n-$C_6H_{13}MgBr$	$Fe(acac)_3$ (5 mol %), THF, –78°, 3 h	 (66)	73
C_5				
		$FeCl_3$ (5 mol %), THF, NMP, –15 to –10°, 5 min	 (96)	89
	RMgBr	Catalyst (5 mol %), additive, THF, 5 min		

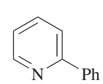
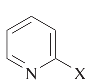
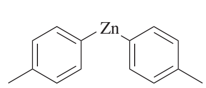
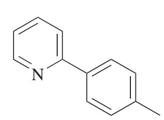
R	Catalyst	Additive	Cosolvent	Temp		Refs.
n-C_6H_{13}	$FeCl_2$	none	none	0°	(85)	43
n-C_6H_{13}	$FeCl_3$	NMP	Et_2O	rt	(88)	85, 43
n-C_6H_{13}	$Fe(acac)_2$	NMP	Et_2O	rt	(90)	85, 43
n-C_6H_{13}	$Fe(acac)_3$	NMP	Et_2O	rt	(91)	85, 43
n-C_6H_{13}	**14**	NMP	Et_2O	rt	(96)	85, 43
Ph	$Fe(acac)_3$	none	none	0°	(73)	43
n-$C_{14}H_{29}$	$Fe(acac)_3$	NMP	Et_2O	rt	(81)	85, 43

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (5 mol %), TMEDA (1.2 eq), Mg (1.2 eq), THF, 0°, 3 h	 X: Cl (38); Br (58)	145
	Ar_2Zn	$FeCl_2(dppbz)_2$ (5 mol %), THF, toluene, 100°, 4 h		99

X	Ar	
2-Cl	2-(4-MeC_6H_4)	(35)
3-Br	3-(4-MeC_6H_4)	(0)
4-Br	4-(4-MeC_6H_4)	(0)

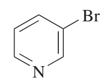
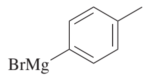
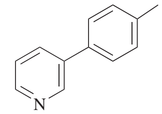
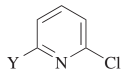
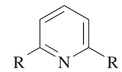
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgBr	1. Catalyst (x mol %), SIPr•HCl (y mol %), EtMgBr (z mol %), THF, 0° 2. rt, 4 h 3. Temp, time		

R	Catalyst	x	y	z	Temp (°)	Time (h)		Refs.
2-thienyl	$FeF_3•3H_2O$	6	18	36	80	24	(74)	93, 94
4-MeC_6H_4	FeF_3	2	6	6	60	16	(66)	94

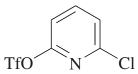
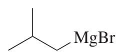
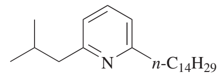
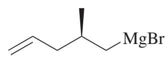
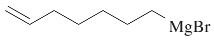
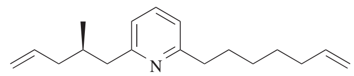
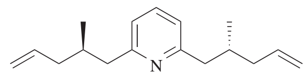
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$Fe(acac)_3$ (10 mol %), THF, –30°, 1 h	 (60)	92
	 (x eq)	$FeCl_2(dppbz)_2$ (5 mol %), 100°, 4 h		99

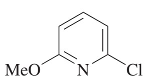
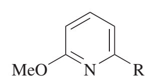
X	x	Solvent	
Br	1.0	THF/toluene	(65)
Br	1.2	THF	(15)
Br	1.2	THF/toluene	(75[a], 53)
I	—	THF/toluene	(55)

TABLE 5. REACTION OF HETEROARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

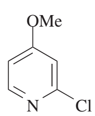
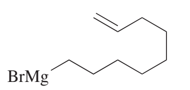
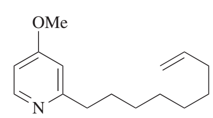
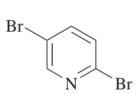
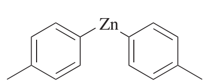
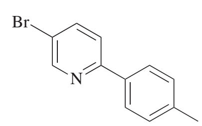
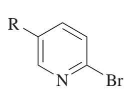
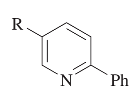
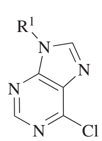
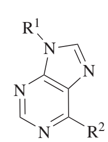
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. FeF_3 (2 mol %), SIPr•HCl (6 mol %), EtMgBr (6 mol %), THE, 0° 2. rt, 4 h 3. 60°, 16 h	 (5)	94
	RMgBr	Catalyst (*x* mol %), THF, NMP, 0°		

Y	R	Catalyst	*x*	Time (min)		Refs.
Cl	n-C_6H_{13}	$Fe(acac)_3$	5	5	(73)	43
TfO	n-C_6H_{13}	$Fe(acac)_3$	5	5	(73)	43
TfO	CH_2=$CH(CH_2)_4$	**14**	10	20	(75)	65

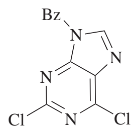
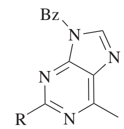
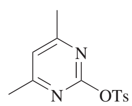
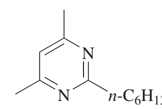
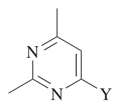
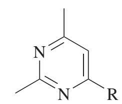
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	 **I** + n-$C_{14}H_{29}MgBr$ **II**	1. $Fe(acac)_3$ (5 mol %), THF, NMP, 0° 2. **I**, 3 min 3. **II**, 5 min	 (71)	43, 87
	 + **I**  **II**	1. Catalyst **14** (10 mol %), THF, NMP, 0° 2. **I**, 20 min 3. **II**, 30 min	 **III** **III** + **IV** (80), **III**/**IV** = 4:1 +  **IV**	65

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgBr	$Fe(acac)_3$ (5 mol %), THF, NMP, 5 min		

R	Cosolvent	Temp		Refs.
i-Pr	none	0°	(56)	43
n-$C_{14}H_{29}$	Et_2O	rt	(95)	85, 43

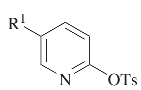
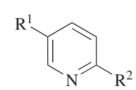
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (5 mol %), THF, Et_2O, NMP, rt, 5 min	 (81)	85, 43, 87
		$FeCl_2(dppbz)_2$ (5 mol %), THF, toluene, 100°, 4 h	 (56[a], 50)	99
C_{5-6}				
	$Na[BPh_4]$	$FeCl_2(dppbz)_2$ (5 mol %), $(4\text{-}MeOC_6H_4)_2Zn$ (10 mol %), THF, toluene, reflux, 16 h	 R Br (49[a], 38) CF_3 (77[a], 53)	99
C_5				
	R^2MgBr	$Fe(acac)_3$ (5 mol %), additive, THF		43

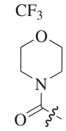
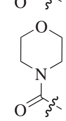
R^1	R^2	Additive	Temp (°)	Time (min)	
H	n-$C_{14}H_{29}$	NMP	0	5	(85)
Me	Ph	none	–30	10	(60)
Me	n-$C_{14}H_{29}$	NMP	0	5	(90)

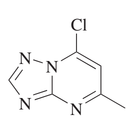
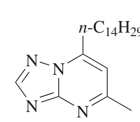
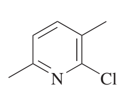
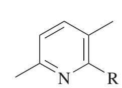
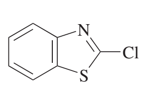
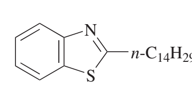
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	MeMgCl (*x* eq)	Fe(acac)$_3$ (10 mol %), additive, THF, rt, 8 h		86
C_6				
	*n*-C_6H_{13}MgBr	$FeCl_3$ (5 mol %), THF, NMP, –15 to –10°, 10 min	 (91)	89
	RMgBr (*x* eq)	Catalyst (*y* mol %)		89

x	Additive	R	
1	none	Cl	(68)
1	NMP	Cl	(72)
3	NMP	Me	(96)

Y	R	*x*	Catalyst	*y*	Solvent	Temp (°)	Time (min)	
TsO	CH_2=CH(CH_2)$_3$	—	$FeCl_3$	5	THF, NMP	–15 to –10	10	(92)
TsO	*c*-C_6H_{11}	—	$FeCl_3$	5	THF, NMP	–15 to –10	15	(77)
(EtO)$_2$PO$_2$	*c*-C_6H_{11}	—	**14**	5	THF, NMP	0	7	(83)
TsO	*n*-C_6H_{13}	1.8	none	—	THF, NMP	–15 to –10	240	not complete
TsO	*n*-C_6H_{13}	1.8	Fe(acac)$_3$	5	THF	–15 to –10	60	not complete
TsO	*n*-C_6H_{13}	1.8	Fe(acac)$_3$	5	DME	–15 to –10	45	(73)
TsO	*n*-C_6H_{13}	1.8	Fe(acac)$_3$	1	THF, NMP	–15 to –10	60	not complete
TsO	*n*-C_6H_{13}	1.8	Fe(acac)$_3$	5	THF, NMP	–15 to –10	15	(88)
TsO	*n*-C_6H_{13}	1.8	FeF_3	5	THF, NMP	–15 to –10	60	—
TsO	*n*-C_6H_{13}	1.8	$FeCl_2$	5	THF, NMP	–15 to –10	15	(94)
TsO	*n*-C_6H_{13}	1.8	$FeCl_3$	5	THF, NMP	–15 to –10	15	(98)
TsO	*n*-C_6H_{13}	1.5	$FeCl_3$	5	THF, NMP	–15 to –10	15	(96)
TsO	*n*-C_6H_{13}	1.3	$FeCl_3$	5	THF, NMP	–15 to –10	20	(90)
(EtO)$_2$PO$_2$	*n*-C_6H_{13}	—	$FeCl_3$	5	THF, NMP	–15 to –10	15	(88)

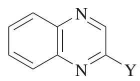
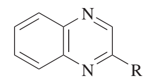
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	R^2MgBr	$FeCl_3$ (5 mol %), THF, NMP, –15 to –10°		89

R^1	R^2	Time (min)	
CF_3	*i*-PrCH$_2$	10	(83)
	CH_2=CH(CH_2)$_3$	15	(76)
	*n*-C_6H_{13}	10	(80)

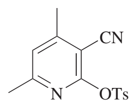
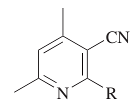
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	*n*-$C_{14}H_{29}$MgBr	Fe(acac)$_3$ (5 mol %), THF, NMP, 0°, 5 min	 (67)	43
C_7				
	RMgBr	Fe(acac)$_3$ (5 mol %), additive, THF		43
	*n*-$C_{14}H_{29}$MgBr	Fe(acac)$_3$ (5 mol %), THF, Et_2O, NMP, rt, 5 min	 (68)	85, 43

R	Additive	Temp (°)	Time (min)	
Ph	none	–30	10	(64)
n-$C_{14}H_{29}$	NMP	0	5	(94)

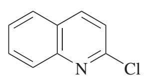
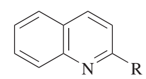
TABLE 5. REACTION OF HETEROARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	R^2MgBr	Catalyst (*x* mol %), additive (*y* eq), THF		

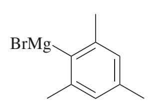
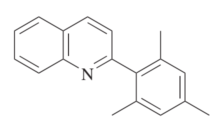
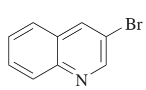
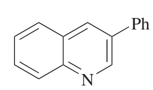
Y	R	Catalyst	*x*	Additive	*y*	Temp (°)	Time (min)		Refs.
Cl	2-thienyl	$Fe(acac)_3$	5	none	—	–30	10	(69)	43
TsO	CH_2=$CH(CH_2)_3$	$FeCl_3$	5	NMP	—	–15 to –10	9	(84)	89
Cl	2-pyridyl	$Fe(acac)_3$	5	NMP	—	0 to rt	7	(82)	43
Cl	3-pyridyl	$Fe(acac)_3$	5	none	—	–30	10	(82)	43
Cl	Ph	**14**	5	none	—	–30	10	(73)	43
Me_2NSO_3	Ph	$Fe(acac)_3$	10	TMEDA	2	–20	10	(81)	89
Cl	*n*-$C_{14}H_{29}$	$Fe(acac)_3$	5	NMP	—	0	5	(95)	43

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgBr	$FeCl_3$ (5 mol %), THF, NMP, –15 to –10°		89

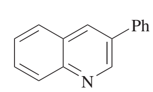
R	Time (min)	
CH_2=$CH(CH_2)_3$	20	(73)
n-C_6H_{13}	15	(85)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	RMgBr	$Fe(acac)_3$ (*x* mol %), THF, –30°		

R	*x*	Time (min)		Refs.
2-thienyl	5	10	(63)	43
3-pyridyl	5	10	(63)	43
Ph	5	10	(71)	43
Ph	10	60	(65)	92

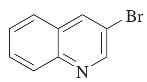
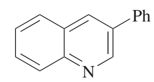
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. FeF_3•$3H_2O$ (3 mol %), SIPr•HCl (9 mol %), EtMgBr (18 mol %), THE, 0° 2. rt, 4 h 3. toluene, 100°, 8 h	 (82)	93, 94
	PhMgBr	Catalyst (10 mol %), 1 h		92

Catalyst	Solvent	Temp	
$Fe(acac)_3$	THF	–78°	(41)
$Fe(acac)_3$	THF	–30°	(46[b], 45)
$Fe(acac)_3$	THF	–20°	(37)
$Fe(acac)_3$	THF	–10°	(32)
$Fe(acac)_3$	THF	0°	(32)
$Fe(acac)_3$	THF	rt	(34)
$Fe(acac)_3$	Et_2O	–30°	(8)
$Fe(acac)_3$	THF/toluene	–30°	(16)
$FeCl_2$	THF	–30°	(9)
$FeCl_3$	THF	–30°	(5)

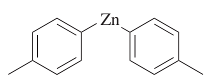
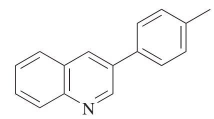
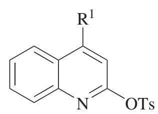
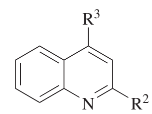
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$Fe(acac)_3$ (10 mol %), additive (*x* mol %), 1 h		92

Additive	*x*	Solvent	Temp (°)	
none	—	THF/NMP	–10	(35)
none	—	THF/TMEDA	–30	(29)
none	—	THF/sulfolane	–30	(36)
none	—	THF/dioxane	–30	(29)
none	—	THF/DMSO	–30	(8)
none	—	THF/DMPU	–30	(13)

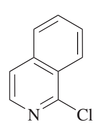
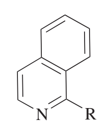
TABLE 5. REACTION OF HETEROARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	PhMgBr	$Fe(acac)_3$ (10 mol %), additive (*x* mol %), 1 h		92

Additive	*x*	Solvent	Temp (°)	
NMP	100	THF	–30	(29)
DMPU	100	THF	–30	(48)
MeCN	100	THF	–30	(16)
bpy	10	THF	–30	(40)
bpy	30	THF	–30	(4)
Me_2S	100	THF	–30	(47)
Ph_3P	50	THF	–30	(38)
$MnCl_2$	20	THF	–30	(9)
$ZnCl_2$	20	THF	–30	(8)
CuCN	20	THF	–30	(8)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_2(dppbz)_2$ (5 mol %), THF, toluene, 100°, 4 h	 (0)	99
$C_{9\text{-}10}$ 	R^2MgBr	$FeCl_3$ (5 mol %), THF, NMP, –15 to –10°		89

R^1	R^2	R^3	Time (min)	
TsO	*i*-Bu	*i*-Bu	10	(76)
MeO_2C	$CH_2{=}CH(CH_2)_3$	MeO_2C	16	(77)
MeO_2C	*n*-C_6H_{13}	MeO_2C	10	(80)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	RMgBr	$Fe(acac)_3$ (5 mol %), additive, THF		43

R	Additive	Temp (°)	Time (min)	
Ph	none	–30	10	(57)
n-$C_{14}H_{29}$	NMP	0	5	(95)

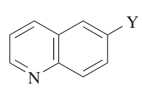
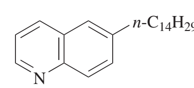
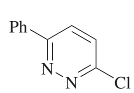
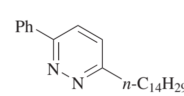
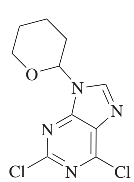
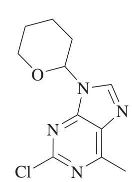
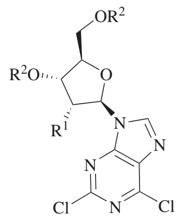
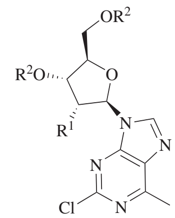
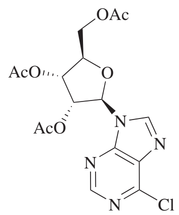
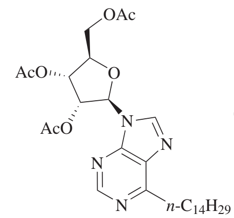
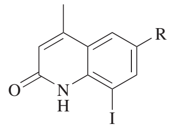
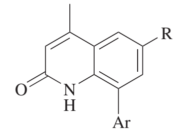
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	*n*-$C_{14}H_{29}$MgBr	$Fe(acac)_3$ (5 mol %), THF, Et_2O, NMP, rt, 5 min	 Y: Cl (92); TfO (74); TsO (82)	85, 43
C_{10} 	*n*-$C_{14}H_{29}$MgBr	$Fe(acac)_3$ (5 mol %), THF, NMP, 0°, 5 min	 (68)	43
	MeMgCl	$Fe(acac)_3$ (10 mol %), additive, THF, rt, 8 h	 Additive: none (57); NMP (67)	86

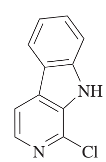
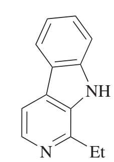
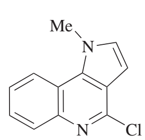
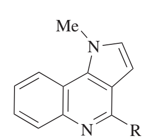
TABLE 5. REACTION OF HETEROARYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	MeMgCl	$Fe(acac)_3$ (10 mol %), additive, THF, rt, 8 h		86

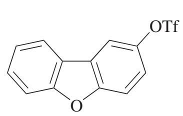
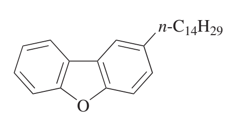
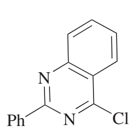
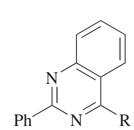
R^1	R^2	Additive	
H	4-MeC_6H_4	none	(50)
H	4-MeC_6H_4	NMP	(61)
BzO	Bz	none	(41)
BzO	Bz	NMP	(60)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	n-$C_{14}H_{29}MgBr$	$Fe(acac)_3$ (5 mol %), THF, NMP, 0°, 5 min	 (72)	43, 87
C_{11}				
	ArCu(CN)MgX	$Fe(acac)_3$ (5 mol %), DME, THF, 80°		97

R	Ar	X	Time (h)	
CF_3	4-$MeOC_6H_4$	Cl	4	(74)
CF_3	4-$MeOC_6H_4$	Cl	12	(84)
CF_3	4-$EtO_2CC_6H_4$	Cl	12	(88)
EtO_2C	4-$MeOC_6H_4$	Br	3	(91)
EtO_2C	4-$EtO_2CC_6H_4$	Cl	3	(96)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	EtMgBr	$Fe(acac)_3$ (5 mol %), THF, NMP, 0°, 5 min	 (67)	43
	RMgX	$Fe(acac)_3$ (5 mol %), THF, NMP, rt, 30 min		88

R	X	
Me	I	(52)
Et	Br	(74)
allyl	Br	trace
i-Pr	Br	(86)
n-Bu	Br	(64)
Ph	Cl	(94)
Bn	Cl	(60)
$Ph(Me_2)C$	Cl	(0)

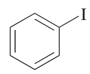
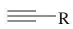
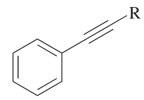
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
	n-$C_{14}H_{29}MgBr$	$Fe(acac)_3$ (5 mol %), THF, Et_2O, NMP, rt, 5 min	 (81)	85, 43, 65
C_{14}				
	RMgBr	$Fe(acac)_3$ (5 mol %), THF, NMP		43

R	Temp (°)	Time (min)	
Ph	–30	10	(66)
n-$C_{14}H_{29}$	0	5	(84)

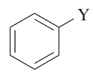
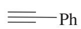
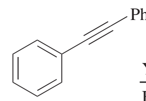
[a] The yield was determined by NMR spectroscopy.

[b] The yield was determined by GLC.

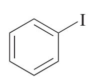
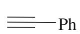
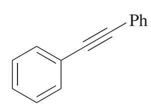
TABLE 6. REACTION OF ARYL ELECTROPHILES WITH ALKYNES

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		Catalyst (x mol %), additive (y mol %), Cs_2CO_3 (2 eq), toluene, 135°		

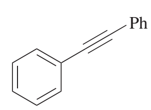
R	Catalyst	x	Additive	y	Time (h)		Refs.
TES	$FeCl_3$	15	DMEDA	30	72	(80)	108
c-C_6H_{11}	$FeCl_3$	15	DMEDA	30	72	(15)	108
4-ClC_6H_4	$Fe(acac)_3$	10	bpy	20	42	(85)	109
4-BrC_6H_4	$Fe(acac)_3$	10	bpy	20	42	(84)	109
3-MeC_6H_4	$FeCl_3$	15	DMEDA	30	72	(51)	108
4-MeC_6H_4	$Fe(acac)_3$	10	bpy	20	42	(89)	109
2-Np	$Fe(acac)_3$	10	bpy	20	42	(86)	109

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (x mol %), DMEDA (y mol %), additive (2 eq), toluene, 135°, 72 h		108

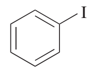
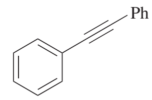
Y	x	y	Additive	
Br	15	30	Cs_2CO_3	trace
I	15	30	Cs_2CO_3	(68)
TsO	15	30	Cs_2CO_3	(0)
I	10	20	K_3PO_4	(37)
I	10	20	t-BuONa	(20)
I	10	20	K_2CO_3	(43)

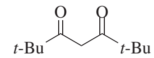
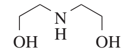
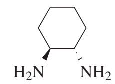
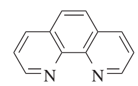
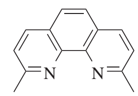
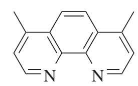
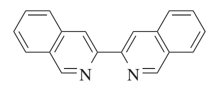
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (10 mol %), DMEDA (20 mol %), Cs_2CO_3 (2 eq), toluene, 135°		108

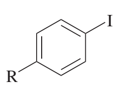
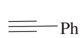
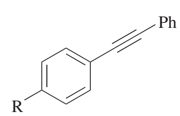
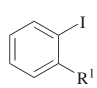
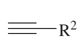
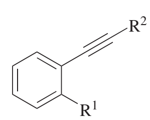
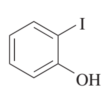
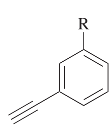
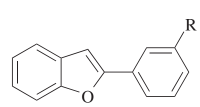
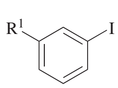
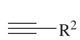
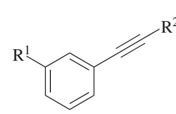
Catalyst	Time (h)	
$FeCl_3$	18	(31)
$FeCl_3$	120	(95)
$Fe(acac)_3$	24	(0)
$FeCl_3•6H_2O$	24	trace
$Fe(bzac)_3$	48	(6)
$Fe(ClO_4)_2$	24	trace

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (10 mol %), bpy (20 mol %), additive (2 eq), toluene, 135°		109

Catalyst	Additive	Time (h)	
$FeCl_3$	Cs_2CO_3	42	(13)
$Fe(O_2CCH{=}CH_2)_3$	Cs_2CO_3	42	(86)
$Fe(acac)_3$	Cs_2CO_3	28	(41)
$Fe(acac)_3$	Cs_2CO_3	42	(90)
$Fe(acac)_3$	Na_2CO_3	42	(<5)
$Fe(acac)_3$	K_3PO_4	42	(37)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		Catalyst (10 mol %), additive (20 mol %), Cs_2CO_3 (2 eq), 135°		

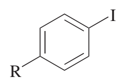
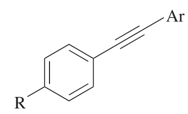
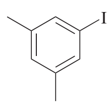
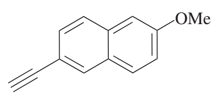
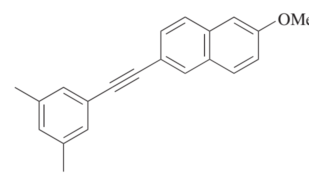
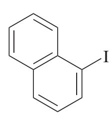
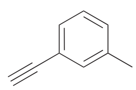
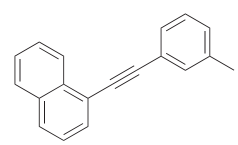
Catalyst	Additive	Solvent	Time (h)	Yield (%)	Refs.
$FeCl_3$	TMEDA	toluene	120	(33)	108
$Fe(acac)_3$	bpy	toluene	42	(85)	109
$FeCl_3$		DMF	24	(0)	108
$FeCl_3$		toluene	24	(0)	108
$FeCl_3$		toluene	24	trace	108
$FeCl_3$		toluene	24	(6)	108
$Fe(acac)_3$	"	toluene	42	(10)	109
$Fe(acac)_3$		toluene	42	(< 5)	109
$Fe(acac)_3$		toluene	42	(15)	109
$Fe(acac)_3$		toluene	42	(< 5)	109

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (15 mol %), DMEDA (30 mol %), Cs_2CO_3 (2 eq), toluene, 135°, 72 h	 R: F (69); O_2N (74)	108
		$FeCl_3$ (15 mol %), DMEDA (30 mol %), Cs_2CO_3 (2 eq), toluene, 135°, 72 h		108
		$FeCl_3$ (15 mol %), DMEDA (30 mol %), Cs_2CO_3 (2 eq), toluene, 135°	 R: H (51); Me (50)	108
C_{6-7}				
		$FeCl_3$ (15 mol %), DMEDA (30 mol %), Cs_2CO_3 (2 eq), toluene, 135°, 72 h		108

R^1	R^2	Yield (%)
Cl	TES	(73)
H_2N	Ph	(89)
BnHN	TES	(85)
BnHN	Ph	(86)
MeO	Ph	(60)
MeO	6-MeO-2-Np	(54)

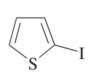
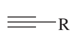
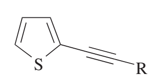
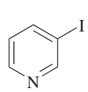
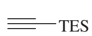
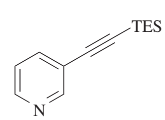
R^1	R^2	Yield (%)
Cl	Ph	(89)
Cl	$3\text{-}MeC_6H_4$	(77)
Me	TES	(90)

TABLE 6. REACTION OF ARYL ELECTROPHILES WITH ALKYNES (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{6-7} 		$Fe(acac)_3$ (10 mol %), bpy (20 mol %), Cs_2CO_3 (2 eq), toluene, 135°, 42 h		109
C_8 		$FeCl_3$ (15 mol %), DMEDA (30 mol %), Cs_2CO_3 (2 eq), toluene, 135°, 72 h	 (99.9)	108
C_{10} 		$FeCl_3$ (15 mol %), DMEDA (30 mol %), Cs_2CO_3 (2 eq), toluene, 135°, 72 h	 (55)	108

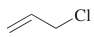
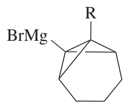
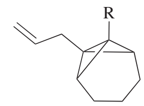
R	Ar	
Br	Ph	(86)
Br	4-BrC_6H_4	(81)
Br	2-Np	(80)
MeO	Ph	(94)
MeO	4-ClC_6H_4	(89)
MeO	4-BrC_6H_4	(86)
MeO	4-MeC_6H_4	(93)
MeO	2-Np	(90)
Me	Ph	(96)
Me	4-ClC_6H_4	(90)
Me	4-MeC_6H_4	(90)
Me	2-Np	(93)

TABLE 7. REACTION OF HETEROARYL ELECTROPHILES WITH ALKYNES

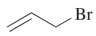
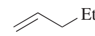
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		Catalyst (x mol %), additive (y mol %), Cs_2CO_3 (2 eq), toluene, 135°		108
C_5 		$FeCl_3$ (15 mol %), DMEDA (30 mol %), Cs_2CO_3 (2 eq), toluene, 135°, 72 h	 (58)	108

R	Catalyst	x	Additive	y	Time (h)	
TES	$FeCl_3$	15	DMEDA	30	72	(40)
Ph	$Fe(acac)_3$	10	bpy	20	42	(87)
4-ClC_6H_4	$Fe(acac)_3$	10	bpy	20	42	(90)
4-MeC_6H_4	$Fe(acac)_3$	10	bpy	20	42	(89)
2-Np	$Fe(acac)_3$	10	bpy	20	42	(87)

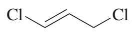
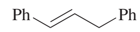
TABLE 8. REACTION OF ALLYLIC ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		$Fe(acac)_3$ (0.5 mol %), 1,4-dioxane, 0°, 3 h		110

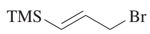
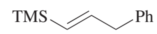
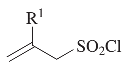
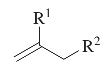
R	
Me	(20)
TMS	(22)
TMSC≡C	(43)
$Me_2C{=}CH$	(31)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	EtMgBr	$FeCl_3$ (0.025 mol %), additive (x eq), THF, rt, 5 min		36

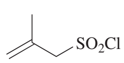
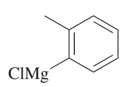
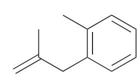
Additive	x	
none	0	(72)
styrene	7.8	(77)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr (x eq)	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min		

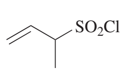
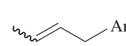
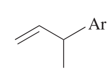
x		Refs.
2.0	(98)	114
2.2	(96)	41

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (97)	114, 41
$C_{3–4}$				
	R^2MgX	$Fe(acac)_3$ (5 mol %), THF, rt		113

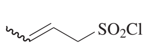
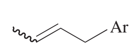
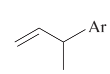
R^1	R^2	X	Time (h)	
H	Ph	Cl	3	(78)
H	$4\text{-}MeOC_6H_4$	Br	3	(91)
H	$n\text{-}C_8H_{17}$	Br	6	(95)
Me	2-thienyl	Br	4	(64)
Me	$c\text{-}C_6H_{11}$	Cl	6	(61)
Me	$4\text{-}FC_6H_4$	Br	4	(74)
Me	$4\text{-}MeC_6H_4$	Br	3	(79)
Me	$4\text{-}Me_2NC_6H_4$	Br	3	(76)
Me	$4\text{-}MeOC_6H_4$	Br	3	(87)
Me	$Ph(CH_2)_2$	Cl	6	(56)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		Catalyst (x mol %), additive		113

Catalyst	x	Additive	Solvent	Temp	Time (h)	
$Fe(acac)_3$	5	none	THF	rt	3	(82)
$Fe(acac)_3$	5	none	THF	reflux	2	(73)
$Fe(acac)_3$	2	none	THF	rt	8	(61)
$Fe(acac)_3$	5	none	DME	rt	2	(75)
$Fe(acac)_3$	5	NMP	THF	rt	3	(78)
$FeCl_3$	5	none	THF	rt	3	(78)
FeF_3	5	none	THF	rt	4	(58)

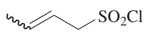
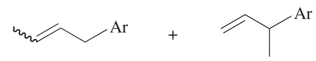
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArMgX	$Fe(acac)_3$ (5 mol %), DME, rt, 4 h	 **I** +  **II**	113

Ar	X	**I + II**	**I/II**	**I** $(E)/(Z)$
$2\text{-}MeC_6H_4$	Cl	(72)	88:12	10:1
$4\text{-}MeC_6H_4$	Cl	(77)	87:13	6:1
$4\text{-}MeOC_6H_4$	Br	(79)	84:16	8:1

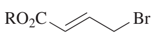
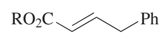
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 $(E)/(Z)$ = 3:1	ArMgX	Catalyst (5 mol %), rt, 4 h	 **I** +  **II**	113

Ar	X	Catalyst	Solvent	**I + II**	**I/II**	**I** $(E)/(Z)$
$2\text{-}MeC_6H_4$	Cl	$Fe(acac)_3$	THF	(78)	86:14	—
$2\text{-}MeC_6H_4$	Cl	$Fe(acac)_3$	toluene	(—)	85:15	—
$2\text{-}MeC_6H_4$	Cl	$Fe(acac)_3$	DME	(75)	90:10	10:1
$2\text{-}MeC_6H_4$	Cl	$Fe(acac)_3$	MeCN	(57)	88:12	—
$2\text{-}MeC_6H_4$	Cl	$Fe(OAc)_2$	THF	(—)	85:15	—

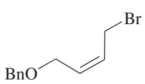
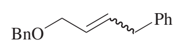
TABLE 8. REACTION OF ALLYLIC ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

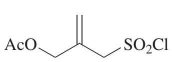
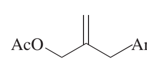
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
 (*E*)/(*Z*) = 3:1 *Continued from previous page.*	ArMgX	Catalyst (5 mol %), rt, 4 h	 I + II	113

Ar	X	Catalyst	Solvent	**I + II**	**I/II**	**I** (*E*)/(*Z*)
2-MeC_6H_4	Cl	$FeCl_3$	THF	(68)	90:10	—
2-MeC_6H_4	Cl	$FeCl_3$	DME	(71)	84:16	—
2-MeC_6H_4	Cl	$FeCl_2$	THF	(—)	87:13	—
2-MeC_6H_4	Cl	$Fe(ClO_4)_2$	THF	(—)	83:17	—
2-MeC_6H_4	Cl	FeF_3	THF	(—)	80:20	—
2-MeC_6H_4	Cl	$FeBr_3$	THF	(—)	90:10	—
2-MeC_6H_4	Cl	$FeBr_2$	THF	(—)	85:15	—
2-MeC_6H_4	Cl	Fe_2O_3	THF	trace	—	—
4-MeC_6H_4	Cl	Fe(acac)$_3$	DME	(82)	88:12	6:1
4-$MeOC_6H_4$	Br	Fe(acac)$_3$	DME	(85)	85:15	8:1

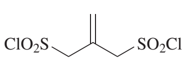
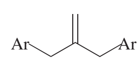
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	Catalyst (*x* mol %), THF		

R	Catalyst	*x*	Temp (°)	Time (min)		Refs.
Me	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	5	–30	<10	(94)	41
Me	$[Li(tmeda)][CpFe(C_2H_4)_2]$	5	–30	30	(45)	41
Me	$Cp^*Fe(C_2H_4)_2$	10	–30	30	(50)	41
Me	(cyclooctenyl)$CpFe(C_2H_4)$	10	–30	30	(46)	41
Me	(allyl)Cp*FeCl	10	–30	30	(73)	41
Et	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	5	–20	5	(94)	114

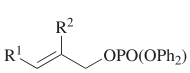
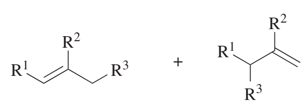
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (80), (*E*)/(*Z*) = 4.4:1	41

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArMgX	Fe(acac)$_3$ (5 mol %), THF		113

Ar	X	
2-MeC_6H_4	Cl	(72)
4-$MeOC_6H_4$	Br	(67)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	ArMgX	Fe(acac)$_3$ (5 mol %), THF, rt, 6 h		113

Ar	X	
Ph	Cl	(75)
2-MeC_6H_4	Cl	(71)
4-$MeOC_6H_4$	Br	(82)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{5–10}$				
	R^3MgX	Fe(acac)$_3$ (5 mol %), THF	 I + II	

R^1	R^2	R^3	X	Temp (°)	Time (h)	**I + II**	**I/II**	Refs.
$TBSOCH_2$	Me	*n*-Bu	Cl	–70	1	(86)	>99:1	111
Ph	H	*n*-Bu	Cl	–70	2	(78)	>99:1	111
n-C_7H_{15}	H	Me	I	–78	1	(87)	97:3	112
n-C_7H_{15}	H	*n*-Bu	Cl	–70	3	(94)	99:1	111
n-C_7H_{15}	H	*n*-Bu	Cl	–78	1	(94)	99:1	112

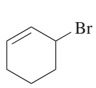
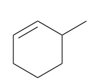
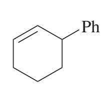
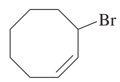
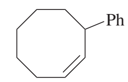
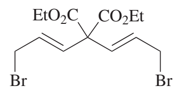
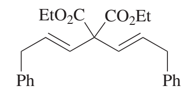
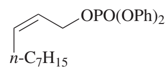
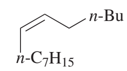
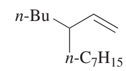
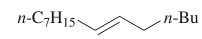
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	Me_3FeLi (5 eq)	Et_2O, –20°, 1 h	 (50)	106
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (95)	41

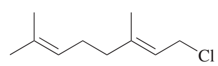
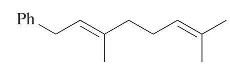
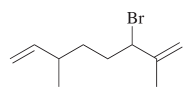
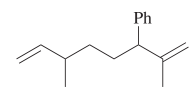
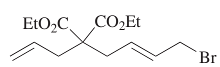
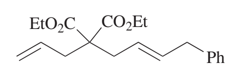
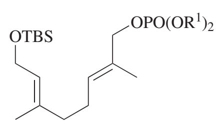
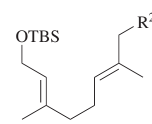
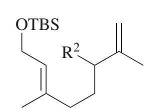
TABLE 8. REACTION OF ALLYLIC ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	PhMgBr	Catalyst (x mol %), THF, –30°		41

Catalyst	x	Time	
$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	5	<20 min	(81)
$[Li(tmeda)][CpFe(C_2H_4)_2]$	5	18 h	(39)
$(cyclooctenyl)CpFe(C_2H_4)$	10	18 h	(33)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (96)	114
C_{10}				
	n-BuMgCl	$Fe(acac)_3$ (5 mol %), THF, –70°	 **I** +  **II** +  **III**	

Time (h)	**I + II + III**	**I/II/III**	Refs.
0.5	(95)	97:3:0	111
1	(93)	92:2:6	112

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (87)	114, 41
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (84)	114, 41
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (93)	114, 41
	R^2MgX	$Fe(acac)_3$ (5 mol %), THF	 **I** +  **II**	111

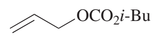
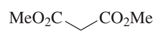
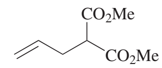
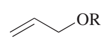
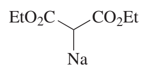
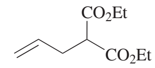
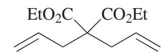
R^1	R^2	X	Temp (°)	Time (h)	**I + II**	**I/II**
Ph	Me	I	–70	0.5	(90)	99:1
Ph	CH_2=CH	Br	–70	2	(54)	91:9
Ph	i-Pr	Br	–70	1.5	(93)	>99:1
Ph	n-Bu	Cl	–70	1.5	(77)	>99:1
Et	Ph	Br	–70	2	(80)	70:30
i-Pr	Ph	Br	–70	2	(68)	73:27
Ph	Ph	Br	–70	0.5	(93)	94:6
Ph	Bn	Br	–45	3	(95)	97:3
Ph	(Z)-1-octenyl	Br	–70	0.5	(94)	84:16
Ph	n-$C_6H_{13}C$	Cl	–70	2	(89)	89:11

TABLE 9. REACTION OF ALLYLIC ELECTROPHILES WITH ACTIVE METHYLENE COMPOUNDS

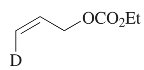
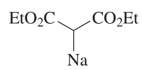
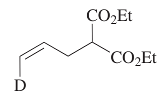
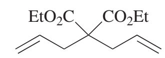
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*

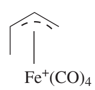
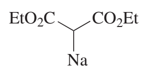
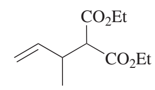
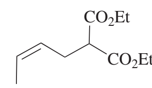
C_3

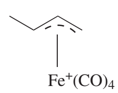
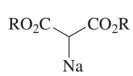
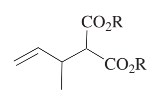
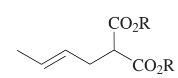
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), PPh_3 (3 mol %), DMF, 80°, 12 h	 (84)	120
		Catalyst (*x* mol %), additive, THF	 **I** +  **II**	

R	Catalyst	*x*	Additive	Temp	Time (h)	**I + II**	**I/II**	Refs.
CHO	$Na[Fe(CO)_3NO]$	25	none	—	4	(88)	**I** only	115
Ac	$Na[Fe(CO)_3NO]$	25	none	—	6	(74)	**I** only	115
Ac	$Fe_2(CO)_9$	10	none	20°	72–120	(74[a], 61)	**I** only	116
EtO_2C	$Bu_4N[Fe(CO)_3NO]$	25	CO	reflux	8	(76)	89:11	122

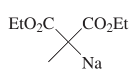
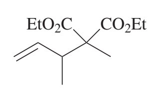
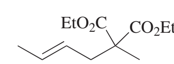
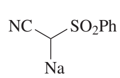
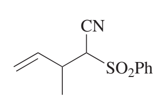
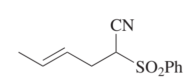
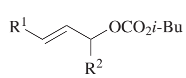
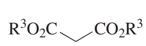
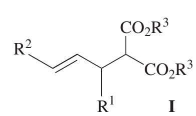
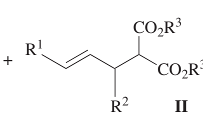
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Bu_4N[Fe(CO)_3NO]$ (25 mol %), THF, CO, reflux, 8 h	 **I** +  **II** **I + II** (—), **I/II** = —	122

C_4

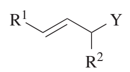
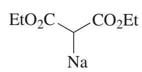
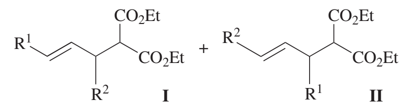
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 20°	 **I** +  **II** **I + II** (—), **I/II** = 17:83	116

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 20°	 **I** +  **II**	

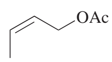
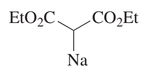
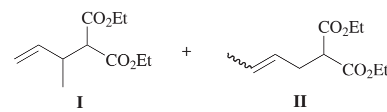
R	Time (h)	**I + II**	**I/II**	Refs.
Me	>1	(—)	43:57	117
Et	—	(—)	52:48	116

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 20°, >1 h	 **I** +  **II** **I + II** (—), **I/II** = 42:58	117
		THF, 20°, >1 h	 **I** +  **II** **I + II** (—), **I/II** = 21:79	117
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), additive (*x* mol %), 80°	 **I** +  **II**	

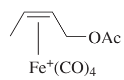
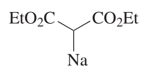
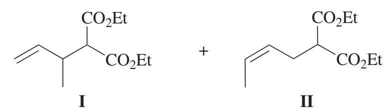
R^1	R^2	R^3	Additive	*x*	Solvent	Time (h)	**I + II**	**I/II**	Refs.
H	Me	Me	PPh_3	3	DMF	24	(78)	98:2	120
H	Me	*i*-Bu	**7c**	2.5	*t*-BuOMe	5	(72[a], 67)	17:83	121
H	Me	*i*-Bu	**7b**	2.5	*t*-BuOMe	5	(78[a], 71)	91:9	121
Me	H	Me	PPh_3	3	DMF	24	(76)	4:96	120
Me	H	*i*-Bu	**7c**	2.5	*t*-BuOMe	5	(72[a], 63)	15:85	121
Me	H	*i*-Bu	**7b**	2.5	*t*-BuOMe	5	(66[a], 64)	12:88	121

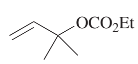
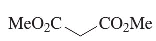
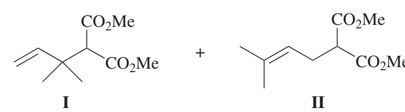
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		Catalyst (*x* mol %), THF		

R^1	R^2	Y	Catalyst	*x*	Additive	Temp	Time (h)	**I** + **II**	**I**/**II**	Refs.
H	Me	Cl	**15**	10	none	—	0.4	(84)	74:26	115
H	Me	Cl	$Na[Fe(CO)_3NO]$	20	none	—	48	(90)	82:28	115
H	Me	AcO	$Na[Fe(CO)_3NO]$	30	none	—	14	(79)	95:5	115
H	Me	AcO	$Fe_2(CO)_9$	10	none	66°	24	(83)	37:63	116
H	Me	EtO_2CO	$Bu_4N[Fe(CO)_3NO]$	25	CO	reflux	10	(78)	93:7	122
Me	H	Cl	$Na[Fe(CO)_3NO]$	20	none	—	48	(79)	10:90	115
Me	H	AcO	$Na[Fe(CO)_3NO]$	10	none	—	14	(90)	9:91	115
Me	H	AcO	$Fe_2(CO)_9$	10	none	20°	48	(—)	58:42	116
Me	H	AcO	$Fe_2(CO)_9$	10	none	66°	24	(62)	64:36	116
Me	H	EtO_2CO	$Bu_4N[Fe(CO)_3NO]$	25	CO	reflux	8	(76)	**II** only	122

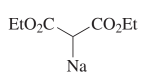
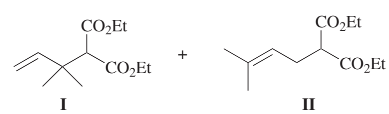
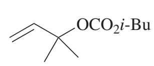
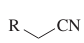
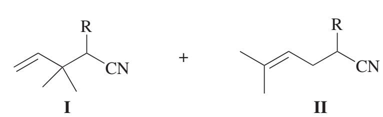
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe_2(CO)_9$ (10 mol %), THF		116

Temp (°)	Time (h)	**I** + **II**	**I**/**II**	**II** (*E*)/(*Z*)
20	96	(78)[a]	69:31	<10:90
66	24	(84)	41:59	(*E*) only

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 20º	 **I** + **II** (—), **I**/**II** = 49:51	116

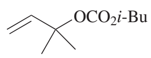
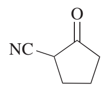
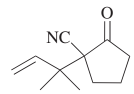
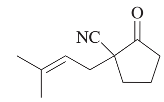
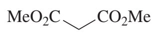
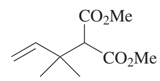
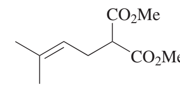
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		$Bu_4N[Fe(CO)_3NO]$ (10 mol %), additive (10 mol %), THF, reflux, 12 h		120

Additive	**I** + **II**	**I**/**II**
none	(8)	—
pyridine	(6)	—
PPh_3	(41)	96:4
PBu_3	(26)	92:8
$P(OEt)_3$	(12)	—
dppe	(8)	—
dppp	(11)	—
dppf	(13)	—

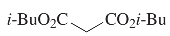
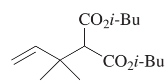
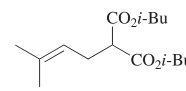
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Bu_4N[Fe(CO)_3NO]$ (25 mol %), THF, CO, reflux, 14 h	 **I** + **II** (78), **I**/**II** = 92:8	122
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), additive (*x* mol %), 80°		

R	Additive	x	Solvent	Time (h)	**I** + **II**	**I**/**II**	Refs.
NC	PPh_3	3	DMF	12	(74)	92:8	120
NC	**7b**	2.5	*t*-BuOMe	5	(85)	99:1	121
NC	**7c**	2.5	*t*-BuOMe	5	(76)	80:20	121
MeO_2C	PPh_3	3	DMF	12	(79)	96:4	120
i-BuO_2C	**7b**	2.5	*t*-BuOMe	5	(88)	95:5	121
i-BuO_2C	**7c**	2.5	*t*-BuOMe	5	(85)	74:26	121
PhO_2S	PPh_3	3	DMF	12	(92)	94:6	120
PhO_2S	**7b**	2.5	*t*-BuOMe	5	(87)	80:20	121
PhO_2S	**7c**	2.5	*t*-BuOMe	5	(86)	60:40	121

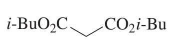
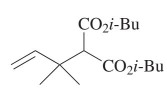
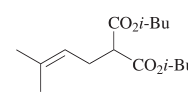
TABLE 9. REACTION OF ALLYLIC ELECTROPHILES WITH ACTIVE METHYLENE COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), PPh_3 (3 mol %), DMF, 80°, 12 h	 **I** +  **II** **I** + **II** (81), **I/II** = 87:13	120
		$Bu_4N[Fe(CO)_3NO]$ (*x* mol %), PPh_3 (*y* mol %)	 **I** +  **II**	120

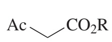
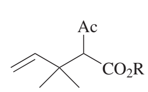
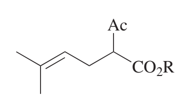
x	*y*	Solvent	Temp	Time (h)	**I + II**	**I/II**
10	10	THF	reflux	12	(68)	96:4
10	10	DME	reflux	12	(43)	92:8
10	10	acetone	reflux	12	(12)	—
10	10	CH_2Cl_2	reflux	12	(0)	—
10	10	toluene	reflux	12	(39)	97:3
10	10	DMSO	reflux	12	(46)	96:4
10	10	MeCN	reflux	12	(60)	58:42
2.5	3	DMF	80°	24	(81)	98:2
10	10	DMF	reflux	12	(95)	98:2
10	10	NMP	reflux	12	(82)	97:3

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), base, additive (2.5 mol %), *t*-BuOMe, 80°, 5 h	 **I** +  **II**	121

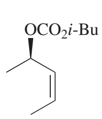
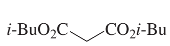
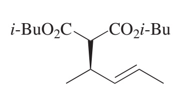
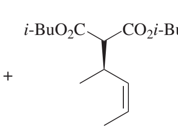
Base	Additive	**I + II**	**I/II**
none	**7b**	(84)	91:9
none	**7c**	(79)	9:91
$Me_2C(Et)OK$	**7c**	(92)	10:90

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), additive (2.5 mol %), base, *t*-BuOMe, 80°, 5 h	 **I** +  **II**	121

Additive	Base	**I + II**	**I/II**
7a	$NaNH_2$	(68)	84:17
7b	$NaNH_2$	(74)	91:9
7d	$NaNH_2$	(66)	87:13
7a	$Me_2C(Et)OK$	(12)	63:37
7b	$Me_2C(Et)OK$	(98)	9:91
7d	$Me_2C(Et)OK$	(38)	33:67

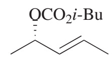
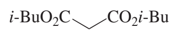
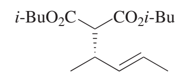
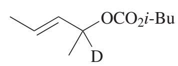
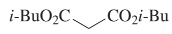
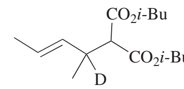
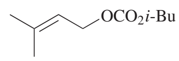
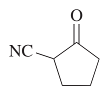
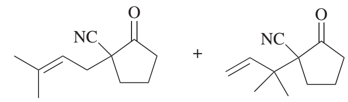
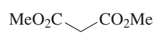
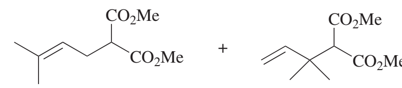
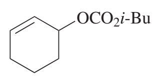
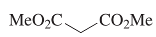
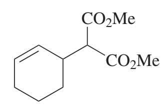
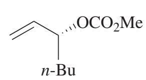
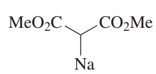
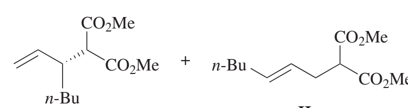
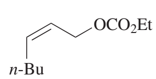
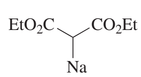
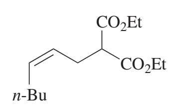
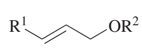
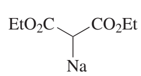
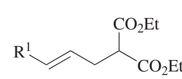
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), additive (*x* mol %), 80°	 **I** +  **II**	

R	Additive	*x*	Solvent	Time (h)	**I + II**	**I/II**	Refs.
Me	PPh_3	3	DMF	24	(71)	96:4	120
i-Bu	**7b**	2.5	*t*-BuOMe	5	(74)	94:6	121
i-Bu	**7c**	2.5	*t*-BuOMe	5	(76)	15:85	121

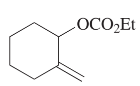
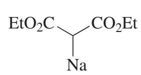
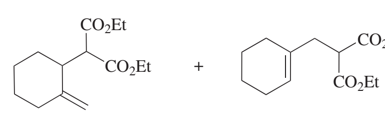
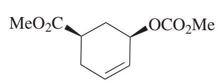
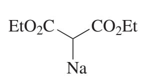
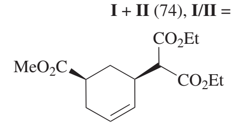
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 er 87:13		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), additive (2.5 mol %), *t*-BuOMe, 80°	 **I** +  **II**	121

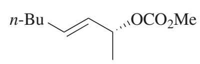
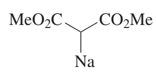
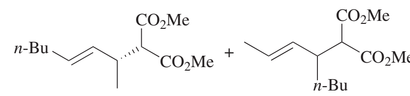
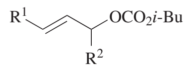
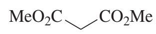
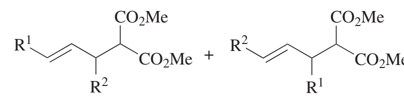
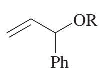
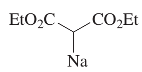
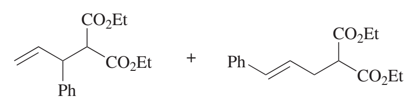
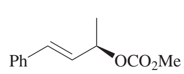
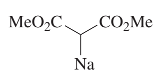
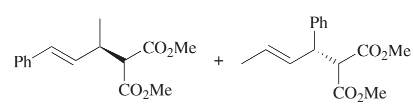
Additive	**I + II**	**I/II**
7b	(78[a], 73)	85:15
7c	(72[a], 72)	13:87

TABLE 9. REACTION OF ALLYLIC ELECTROPHILES WITH ACTIVE METHYLENE COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
 er 91.5:8.5		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), additive (2.5 mol %), *t*-BuOMe, 80°	 Additive / er **7b** (79) 88:12 **7c** (74) 56:44	121
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), additive (2.5 mol %), *t*-BuOMe, 80°	 Additive / % D **7b** (72) 92 **7c** (65) 57	121
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), PPh_3 (3 mol %), DMF, 80°, 24 h	 **I** + **II** **I** + **II** (65), **I/II** = 84:16	120
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), PPh_3 (3 mol %), DMF, 80°, 48 h	 **I** + **II** **I** + **II** (61), **I/II** = 93:7	120
C_6				
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), PPh_3 (3 mol %), DMF, 80°, 48 h	 (69)	120
C_7				
 er >97.5:2.5		$Bu_4N[Fe(CO)_3NO]$ (25 mol %), THF, CO, reflux, 14 h	 **I** er >97.5:2.5 + **II** **I** + **II** (76), **I/II** = 80:20	119
 (*E*)/(*Z*) = 9:91		$Bu_4N[Fe(CO)_3NO]$ (25 mol %), THF, CO, reflux, 10 h	 (83), (*E*)/(*Z*) = 13:87	122
$C_{7–9}$				
		Catalyst (*x* mol %), additive, THF		

R^1	R^2	Catalyst	*x*	Additive	Temp	Time (h)		Refs.
n-Bu	EtO_2C	$Bu_4N[Fe(CO)_3NO]$	25	CO	reflux	8	(85)	122
Ph	Ac	$Na[Fe(CO)_3NO]$	10	none	—	14	(91)	115
Ph	EtO_2C	$Bu_4N[Fe(CO)_3NO]$	25	CO	reflux	10	(82)	122

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		$Bu_4N[Fe(CO)_3NO]$ (25 mol %), THF, CO, reflux, 12 h	 **I** + **II** **I** + **II** (74), **I/II** = 64:36	122
		$Bu_4N[Fe(CO)_3NO]$ (25 mol %), THF, CO, reflux, 8 h	 (75)	122

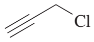
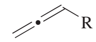
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
 er >97.5:2.5		$Bu_4N[Fe(CO)_3NO]$ (25 mol %), THF, CO, reflux	 **I** er >97.5:2.5 **II** **I** + **II** (84), **I/II** = 95:5	119
C_9				
		$Bu_4N[Fe(CO)_3NO]$ (2.5 mol %), PPh_3 (3 mol %), DMF, 80°	 **I** **II**	120
		Catalyst (*x* mol %), additive, THF	 **I** **II**	
C_{10}				
 er 87.5:12.5		$Bu_4N[Fe(CO)_3NO]$ (25 mol %), THF, CO, reflux, 12 h	 **I** er 87.5:12.5 **II** er 87.5:12.5 **I** + **II** (78), **I/II** = 93:7	119

R^1	R^2	Time (h)	**I** + **II**	**I/II**
H	Ph	24	(78)	98:2
Ph	H	48	(56)	92:8
Ph	Ph	48	(53)	—

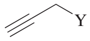
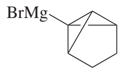
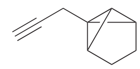
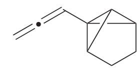
R	Catalyst	*x*	Additive	Temp	Time (h)	**I** + **II**	**I/II**	Refs.
Ac	$Na[Fe(CO)_3NO]$	30	none	—	24	(83)	66:34	115
EtO_2C	$Bu_4N[Fe(CO)_3NO]$	25	CO	reflux	12	(76)	75:25	122

[a] The yield was determined by GLC.

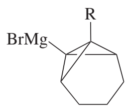
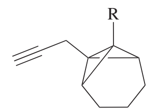
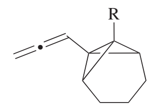
TABLE 10. REACTION OF PROPARGYLIC ELECTROPHILES WITH ORGANOMAGNESIUM COMPOUNDS

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	RMgBr	$FeCl_3$, THF, rt		127

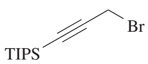
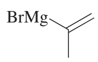
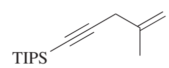
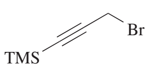
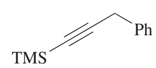
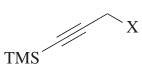
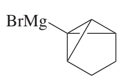
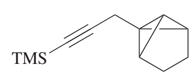
R	Time (min)	
n-Bu	10	(85)
s-Bu	60	(70)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), 1,4-dioxane, 0°, 3 h	 **I** +  **II**	110

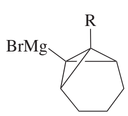
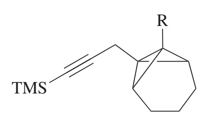
Y	Catalyst	*x*	**I + II**	**I/II**
Cl	$FeCl_3$	0.5–1	(18)	50:50
Cl	$Fe(acac)_3$	0.5	(50)	60:40
Cl	$Fe(acac)_3$	0.5–1	(47)	58:42
Cl	$Fe(dbm)_3$	0.5–1	(18)	59:41
TsO	$Fe(acac)_3$	0.5	(47)	20:80

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (0.5 mol %), 1,4-dioxane, 0°, 3 h	 **I** +  **II**	110

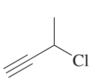
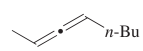
Y	R	**I + II**	**I/II**
TsO	H	(47)	25:75
Cl	CH_2=(Me)C	(69)	36:64
Cl	Me_2C=(Me)C	(30)	40:60

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $FeCl_3$ (10 mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0°, 0.5 h	 (80)	47
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (96)	114, 41
		$Fe(acac)_3$ (0.5 mol %), 1,4-dioxane, 0°, 3 h		110

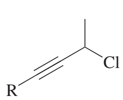
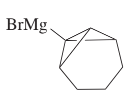
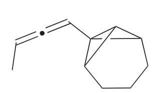
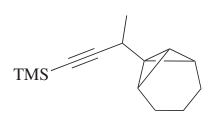
X	
Cl	(7)
Br	(20)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (0.5 mol %), 1,4-dioxane, 0°, 3 h		110

X	R	
Cl	H	(41)
Br	H	(17)
Cl	TMS	(32)
Cl	Me	(37)
Cl	TMSC≡C	(49)
Cl	CH_2=(Me)C	(68)
Cl	Me_2C=CH	(53)

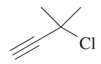
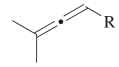
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	*n*-BuMgBr	$FeCl_3$		

Solvent	Temp	Time (min)		Refs.
THF	rt	10	(80)	127
THF/Et_2O	0°	15	(90)	126

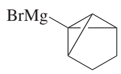
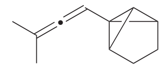
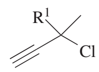
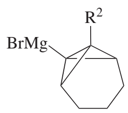
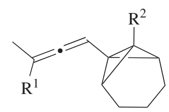
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (0.5 mol %), 1,4-dioxane, 0°, 3 h	 **I** +  **II**	110

R	**I + II**	**I/II**
H	(27)	**I** only
TMS	(48)	**II** only

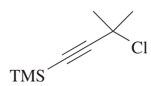
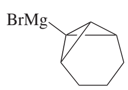
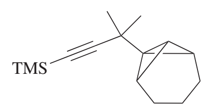
TABLE 10. REACTION OF PROPARGYLIC ELECTROPHILES WITH ORGANOMAGNESIUM COMPOUNDS (*Continued*)

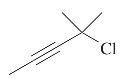
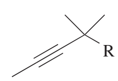
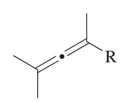
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	RMgX	See table		

R	X	Catalyst	Solvent	Temp	Time (min)		Refs.
Et	I	$FeCl_3$	THF	rt	10	(80)	127
n-Bu	Br	$FeCl_3$	THF	rt	10	(80–90)	127
n-Bu	—[a]	$FeCl_3$	THF/Et_2O	0°	15	(80)	126
n-Bu	Br	$Fe(acac)_3$	THF	rt	30	(60)	127
s-Bu	Br	$FeCl_3$	THF	rt	60	(75)	127

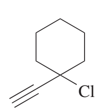
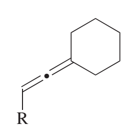
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (0.5 mol %), 1,4-dioxane, 0°, 3 h	 (36)	110
$C_{5\text{-}6}$ 		$Fe(acac)_3$ (0.5 mol %), 1,4-dioxane, 0°, 3 h		110

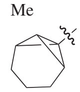
R^1	R^2	
Me	H	(37)
Me	TMS	(40)
Me	Me	(14)
Me	TMSC≡C	(50)
Me	Me_2C=CH	(54)
Me	*t*-BuC≡C	(61)
Et	H	(39)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		$Fe(acac)_3$ (0.5 mol %), 1,4-dioxane, 0°, 3 h	 (3)	110

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	RMgX	See table	 + 	

R	X	Catalyst	Solvent	Temp	Time (min)	**I + II**	**I/II**	Refs.
Me	I	$FeCl_3$	THF	rt	10	(90)	50:50	127
Me	—[a]	$FeCl_3$	THF/Et_2O	0°	15	(40–43)	50:50	126
i-Pr	Br	$FeCl_3$	THF	rt	60	(88)	**II** only	127
i-Pr	—[a]	$FeCl_3$	THF/Et_2O	0°	15	(88)	—	126
n-Bu	Br	$FeCl_3$	THF	rt	20	(87)	**II** only	127
n-Bu	—[a]	$FeCl_3$	THF/Et_2O	0°	15	(87)	—	126
n-Bu	Br	$FeBr_2$	THF	—	20	(80)	**II** only	127
t-Bu	Br	$FeCl_3$	THF	rt	240	(0)	—	127

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	RMgX	See table		

R	X	Catalyst	Solvent	Temp (°)	Time (h)		Refs.
Me	—[a]	$FeCl_3$	THF/Et_2O	0	0.25	(84)	126
	Br	$Fe(acac)_3$(0.5 mol %)	1,4-dioxane	0	3	(36)	110

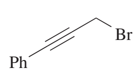
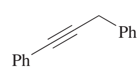
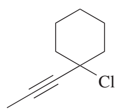
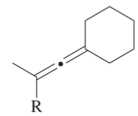
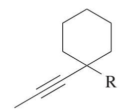
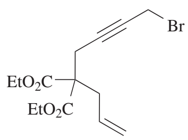
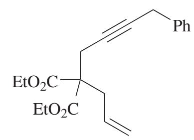
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (93)	114, 41

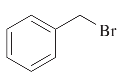
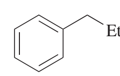
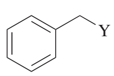
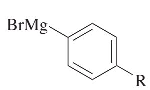
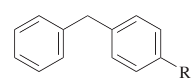
TABLE 10. REACTION OF PROPARGYLIC ELECTROPHILES WITH ORGANOMAGNESIUM COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	RMgX	$FeCl_3$	 **I** +  **II**	
C_{10}				
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (87)	114, 41

R	X	Solvent	Temp	Time (min)	**I + II**	**I/II**	Refs.
Me	I	THF	rt	10	(90)	50:50	127
Me	—[a]	THF/Et_2O	0°	15	(45)	50:50	126
n-Bu	—[a]	THF/Et_2O	0°	15	(70–80)	**I** only	126

[a] X was not specified.

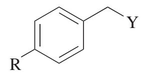
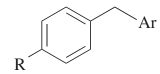
TABLE 11. REACTION OF BENZYLIC ELECTROPHILES WITH MISCELLANEOUS COMPOUNDS

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	EtMgBr	$FeCl_3$ (0.025 mol %), additive (*x* eq), THF, rt		36
		Catalyst (5 mol %), additive (*x* mol %)		

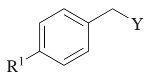
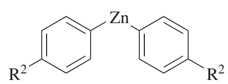
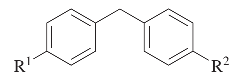
Additive	*x*	Time (min)	
none	—	10	(4)
styrene	7.8	5	(1)

Y	R	Catalyst	Additive	*x*	Solvent	Temp	Time (h)		Refs.
Cl	H	$Cp(PMe_2Ph)_2FeBr$	none	—	toluene	rt	24	(3)	95
Cl	H	$Cp(PMe_2Ph)_2FeBr$	none	—	Et_2O	rt	4	(3)	95
Cl	H	Cp(dmpe)FeBr	none	—	toluene	rt	3	(1)	95
Cl	H	Cp(dppe)FeBr	none	—	toluene	rt	100	(11)	95
Cl	H	$(dppe)FeBr_2$	none	—	Et_2O	rt	24	(12)	95
Cl	H	$Cp(PMe_2Ph)(CO)FeBr$	none	—	Et_2O	rt	24	(3)	95
Cl	H	$Cp(PPh_3)(CO)FeBr$	none	—	Et_2O	rt	24	(10)	95
Cl	H	$Cp(PMe_2Ph)_2FePh$	none	—	benzene	rt	4	(5)	95
Cl	H	Cp(dmpe)FePh	none	—	Et_2O	rt	4	(2)	95
Cl	H	$FeCl_3$	none	—	THF	rt	48	(21)	95
Cl	H	$FeCl_3$	none	—	toluene	rt	12	(12)	95
Cl	H	$FeCl_3$	PMe_2Ph	10	toluene	rt	24	(23)	95
Cl	H	$FeCl_2•H_2O$	PMe_2Ph	10	toluene	rt	12	(36)	95
Cl	H	$FeBr_2$	PMe_2Ph	10	toluene	rt	12	(29)	95
Br	H	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	none	—	THF	–20°	5 min	(62)	41
ClO_2S	H	$Fe(acac)_3$	NMP	—	THF	80°	2[a]	(55)	61
ClO_2S	Me	$Fe(acac)_3$	NMP	—	THF	80°	2[a]	(58)	61

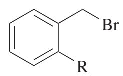
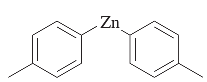
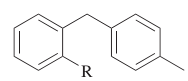
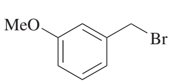
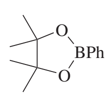
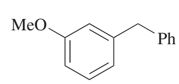
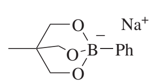
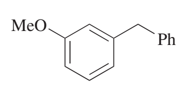
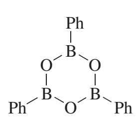
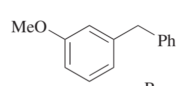
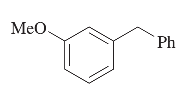
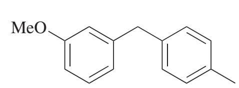
TABLE 11. REACTION OF BENZYLIC ELECTROPHILES WITH MISCELLANEOUS COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	Na[BAr$_4$]	$FeCl_2(dppbz)_2$ (5 mol %), $(4\text{-}MeOC_6H_4)_2Zn$ (10 mol %), toluene, THF, 85°		99

R	Y	Ar	Time (h)	
H	Br	Ph	4	(91[b], 63)
H	$(EtO)_2PO_2$	Ph	24	(14)
H	Br	$4\text{-}ClC_6H_4$	4	trace
H	Br	$4\text{-}MeC_6H_4$	4	(96)
Br	Br	Ph	4	(95[b], 79)
O_2N	Br	Ph	4	(0)

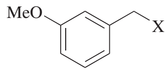
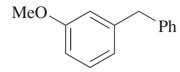
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{7-8} 		$FeCl_2(dppbz)_2$ (5 mol %), toluene, 45°		129

R^1	Y	R^2	Time (h)	
H	Cl	Me	4	(78)
H	Br	Me	4	(>99[b], 76)
H	$(EtO)_2PO_2$	Me	24	(75)
H	Br	CF_3	4	(97[b], 58)
H	Br	MeO	4	(>99[b], 95)
Br	Br	Me	4	(>99[b], 80)
Br	$(EtO)_2PO_2$	Me	24	(73)
MeO	Br	MeO	4	(80[b], 64)
Me	Cl	Me	4	(82)
Me	Br	Me	4	(>99[b], 86)
Me	Br	CF_3	4	(95)
Me	Br	MeO	4	(>99)
CF_3	Br	Me	4	(98[b], 59)
MeO_2C	Br	Me	4	(95[b], 69)

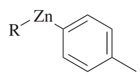
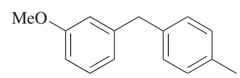
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_2(dppbz)_2$ (5 mol %), toluene, 45°, 4 h	 R: Br (93[b], 81); CF_3 (85[b], 64); NC (90[b], 73)	129
C_7 	$PhB(OH)_2$ or 	$FeCl_2(dppbz)_2$ (5 mol %), $(4\text{-}MeOC_6H_4)_2Zn$ (10 mol %), additive, toluene, THF, 85°, 4 h	 Additive: none (0); K_2CO_3 (0)	99
		$FeCl_2(dppbz)_2$ (5 mol %), $(4\text{-}MeOC_6H_4)_2Zn$ (10 mol %), toluene, THF, 85°, 4 h	 (0)	99
		$FeCl_2(dppbz)_2$ (5 mol %), R_2Zn (*x* mol %), additive, toluene, THF, 85°, 4 h		99
	Li[$PhBBu_3$]	$FeCl_2(dppbz)_2$ (5 mol %), $(4\text{-}MeOC_6H_4)_2Zn$ (10 mol %), toluene, THF, 85°, 4 h	 (49)	99
	K[$4\text{-}MeC_6H_4BF_3$]	$FeCl_2(dppbz)_2$ (5 mol %), $(4\text{-}MeOC_6H_4)_2Zn$ (10 mol %), toluene, THF, 85°, 4 h	 (0)	99

R	*x*	Additive	
Et	5	none	(17)
$4\text{-}MeOC_6H_4$	10	none	(0)
$4\text{-}MeOC_6H_4$	10	K_2CO_3	(0)

TABLE 11. REACTION OF BENZYLIC ELECTROPHILES WITH MISCELLANEOUS COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	$Na[BPh_4]$	Catalyst (x mol %), additive (y mol %)		99

X	Catalyst	x	Additive	y	Solvent	Temp (°)	Time (h)	
Cl	$FeCl_2(dppbz)_2$	5	$(4\text{-}MeOC_6H_4)_2Zn$	10	toluene/THF	85	4	(75)
Br	$Fe(acac)_3$	5	$(4\text{-}MeOC_6H_4)_2Zn$	10	toluene/THF	85	4	(24)
Br	$FeCl_2py_4$	5	$(4\text{-}MeOC_6H_4)_2Zn$	10	toluene/THF	85	4	(59)
Br	$FeCl_2dppp$	5	$(4\text{-}MeOC_6H_4)_2Zn$	10	toluene/THF	85	4	(44)
Br	$FeCl_2(dppbz)_2$	5	none	—	toluene/THF	85	4	(0)
Br	$FeCl_2(dppbz)_2$	5	$ZnCl_2$	10	toluene/THF	85	4	(48)
Br	$FeCl_2(dppbz)_2$	5	Et_2Zn	10	toluene/THF	85	4	(29)
Br	$FeCl_2(dppbz)_2$	1	$(4\text{-}MeOC_6H_4)_2Zn$	10	toluene/THF	reflux	16	(71)
Br	$FeCl_2(dppbz)_2$	2.5	$(4\text{-}MeOC_6H_4)_2Zn$	10	toluene/THF	85	4	(93)
Br	$FeCl_2(dppbz)_2$	5	$(4\text{-}MeOC_6H_4)_2Zn$	5	toluene/THF	85	4	(96)
Br	$FeCl_2(dppbz)_2$	5	$(4\text{-}MeOC_6H_4)_2Zn$	10	THF	85	4	(0)
Br	$FeCl_2(dppbz)_2$	5	$(4\text{-}MeOC_6H_4)_2Zn$	10	toluene/THF	85	4	(96[b], 88)
Br	$FeCl_2(dppbz)_2$	5	$(4\text{-}MeC_6H_4)_2Zn$	10	toluene/THF	85	4	(95)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	 (x eq)	Catalyst (5 mol %), toluene		129

X	R	x	Catalyst	Temp (°)	Time (h)	
Cl	$4\text{-}MeC_6H_4$	—	$FeCl_2(dppbz)_2$	45	4	(83)
Br	$TMSCH_2$	—	$FeCl_2(dppbz)_2$	45	24	(74)
Br	$4\text{-}MeC_6H_4$	0.5	$FeCl_2(dppbz)_2$	45	4	(49)
Br	$4\text{-}MeC_6H_4$	0.5	$FeCl_2(dppbz)_2$	45	16	(50)
Br	$4\text{-}MeC_6H_4$	2	$FeCl_2(dppbz)_2$	45	24	(50)
Br	$4\text{-}MeC_6H_4$	—	$FeCl_2(dppbz)_2$	rt	4	(71)
Br	$4\text{-}MeC_6H_4$	—	$FeCl_2(dppbz)_2$	45	4	(94[b], 92)
Br	$4\text{-}MeC_6H_4$	—	$FeCl_2(dppbz)$	45	4	(80)
Br	$4\text{-}MeC_6H_4$	—	$FeCl_2(dppbz)$	45	16	(86)
Br	$4\text{-}MeC_6H_4$	—	$FeCl_2(dppp)$	45	4	(71)

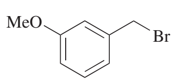
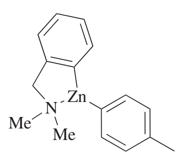
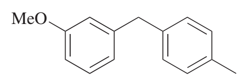
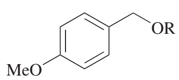
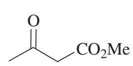
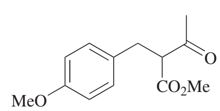
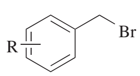
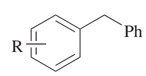
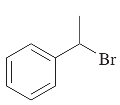
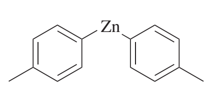
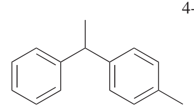
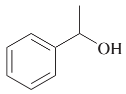
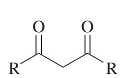
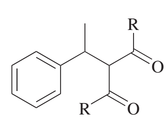
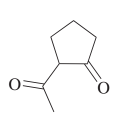
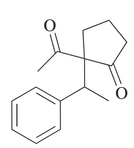
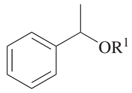
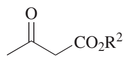
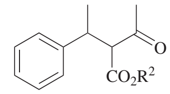
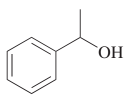
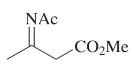
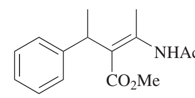
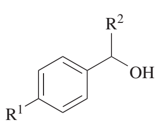
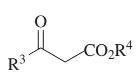
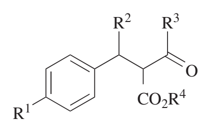
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_2(dppbz)_2$ (5 mol %), toluene, 45°, 24 h	 (89)	129
		$FeCl_3$•$6H_2O$ (5 mol %), $MeNO_2$, 50°, 4 h	 R: H (44); Ac (66)	128
C_8				
	$Na[BPh_4]$	$FeCl_2(dppbz)_2$ (5 mol %), $(4\text{-}MeOC_6H_4)_2Zn$ (10 mol %), toluene, THF, 85°, 4 h	 R: 4-Me (90[b], 61); 3-CF_3 (>99); 4-CF_3 (>99); 2-NC (85[b], 73); 4-MeO_2C (98[b], 80)	99
		$FeCl_2(dppbz)_2$ (5 mol %), toluene, 45°, 4 h	 (0)	129
		$FeCl_3$•$6H_2O$ (5 mol %), $MeNO_2$, 50°, 4 h	 R: Me (99); Ph (99)	128
		$FeCl_3$•$6H_2O$ (5 mol %), $MeNO_2$, 50°, 4 h	 (77)	128

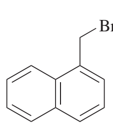
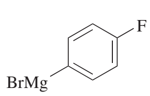
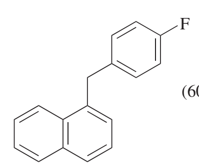
TABLE 11. REACTION OF BENZYLIC ELECTROPHILES WITH MISCELLANEOUS COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8  **I**	 **II**	$FeCl_3$•$6H_2O$ (x mol %)		128

R^1	R^2	**I/II**	x	Solvent	Temp (°)	Time (h)	
H	Me	—	10	none	100	20	(99)
H	Me	1:20	10	$MeNO_2$	50	20	(99)
H	Me	1:20	10	$MeNO_2$	rt	20	(48)
H	Me	1:20	10	$MeNO_2$	50	6	(99)
H	Me	1:20	10	$MeNO_2$	50	2	(95)
H	Me	1:20	10	$MeNO_2$	50	1	(66)
H	Me	1:10	10	$MeNO_2$	50	20	(95)
H	Me	1:4	10	$MeNO_2$	50	20	(90)
H	Me	1:1	10	$MeNO_2$	50	20	(61)
H	Me	4:1	10	$MeNO_2$	50	20	(79)
H	Me	10:1	10	$MeNO_2$	50	20	(51)
H	Me	20:1	10	$MeNO_2$	50	20	(28)
H	Me	1:10	5	CH_2Cl_2	50	2	(47)
H	Me	1:10	5	$MeNO_2$	50	2	(99)
H	Me	1:4	5	$MeNO_2$	50	4	(98)
H	Me	1:20	1	$MeNO_2$	50	4	(12)
Ac	Me	—	5	$MeNO_2$	50	4	(99)
H	Et	—	5	$MeNO_2$	50	4	(97)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$•$6H_2O$ (10 mol %), $MeNO_2$, 50°, 20 h	 (38)	128
$C_{8–13}$ 		$FeCl_3$•$6H_2O$ (x mol %), $MeNO_2$, 50°		128

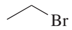
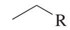
R^1	R^2	R^3	R^4	x	Temp (°)	Time (h)	
H	Me	Et	Me	5	50	4	(95)
H	Me	Ph	Et	10	50	20	(99)
Cl	Me	Me	Me	5	50	4	(82)
H	Et	Me	Me	5	50	4	(51)
H	Et	Me	Me	10	80	20	(60)
H	Ph	Me	Me	5	50	4	(99)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		bmim-$FeCl_4$ (5 mol %), Et_2O, 0°, 10 min	 (60)	133

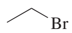
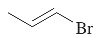
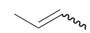
[a] The addition was carried out at 2mL/h.

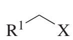
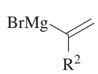
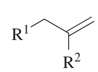
[b] The yield was determined by NMR spectroscopy.

TABLE 12A. REACTION OF ALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

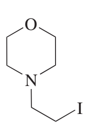
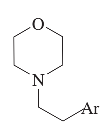
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_1				
MeBr	n-PrMgBr	$FeCl_3$ (0.025 mol %), THF, 2°, 20 min	n-C_4H_{10} (0)[a]	36
C_2				
EtBr	MeMgBr	$Fe(dbm)_3$ (0.33 mol %), THF	n-C_3H_8 (16)[a] + n-C_4H_{10} (8)[a]	52
	RMgBr	Catalyst (x mol %), additive (y eq)		

R	Catalyst	x	Additive	y	Solvent	Temp	Time		Refs.
Et	$FeCl_3$	0.08	none	—	none	2°	—	(<0.1)	5
Et	$FeCl_3$	0.025	none	—	THF	2°	31 min	(—)	36
n-Pr	$FeCl_3$	0.025	none	—	THF	2°	45 min	(0)[a]	36
i-Pr	$FeCl_3$	0.00625	none	—	THF	2°	4 h	(0)[a]	36
(E)-MeCH=CH	$Fe(dbm)_3$	0.3–0.4	none	—	THF	rt	1.5–8 h	(19–33)[a]	36
t-$BuCH_2$	$FeCl_3$	5	none	—	THF	rt	10 min	(7)[a]	36
t-$BuCH_2$	$FeCl_3$	0.025	none	—	THF	rt	4 h	(1)[a]	36
Ph	$FeCl_3$	5	none	—	THF	rt	5 min	(21)[a]	36
Ph	$FeCl_3$	0.025	none	—	THF	rt	24 h	(1)[a]	36
Bn	$FeCl_3$	5	none	—	THF	rt	1 h	(4)[a]	36
Bn	$FeCl_3$	0.025	none	—	THF	rt	30 min	(3)[a]	36
Bn	$FeCl_3$	0.025	styrene	7.8	THF	rt	30 min	(5)[a]	36

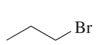
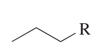
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-3}				
 + 	MeMgBr	$Fe(dbm)_3$ (0.33 mol %), THF	C_3H_8 (3)[a] +  (52)[a] + n-C_4H_{10} (0.4)[a]	36

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{2-12}				
		1. $FeCl_3$ (x mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0°, 30 min		47

R^1	X	R^2	x	
$(EtO)_2CH$	Br	Me	5	(50)
t-BuO_2C	Br	Me	5	(—)
EtO_2CCH_2	Br	Me	10	(—)
$TBDPSOCH_2(Me)CH$	I	TMS	5	(29)
$TBDPSOCH_2(Me)CH$	I	Me	10	(87)
$EtO_2C(CH_2)_3$	Br	TMS	10	(40)
$EtO_2C(CH_2)_3$	Br	Me	10	(62)
n-C_5H_{11}	Cl	Me	10	(—)
CH_2=$CH(CH_2)_3$	I	TMS	10	(77)
CH_2=$CH(CH_2)_3$	I	Me	10	(35)
n-$C_{11}H_{23}$	Br	TMS	10	(52)
n-$C_{11}H_{23}$	Br	Me	10	(82)

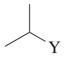
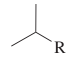
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
	ArMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min		

Ar		Refs.
Ph	(87)	114, 41
4-PhC_6H_4	(85)	114

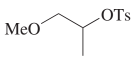
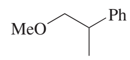
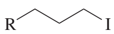
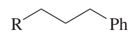
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	RMgBr	$FeCl_3$ (x mol %), THF		36

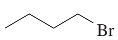
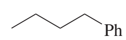
R	x	Temp	Time	
Me	5	2°	7 h	(5)
Me	0.025	rt	7 h	(11)
Et	5	2°	2.5 min	(0)[a]
Et	0.025	2°	27 min	(0)[a]
Et	0.0025	2°	3 h	(0)[a]
n-Pr	0.025	2°	55 min	(—)[a]

TABLE 12A. REACTION OF ALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

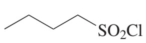
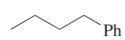
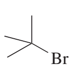
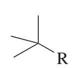
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	RMgBr	Catalyst (*x* mol %)		

Y	R	Catalyst	*x*	Solvent	Temp	Time		Refs.
Br	Me	$FeCl_3$	5	THF	rt	15 min	(10)[a]	36
Br	Me	$FeCl_3$	0.025	THF	rt	3 h	(15)[a]	36
Br	Et	$FeCl_3$	5	THF	2°	2.5 min	(0)[a]	36
Br	Et	$FeCl_3$	0.125	THF	2°	10 min	(0)[a]	36
Br	Et	$FeCl_3$	0.00625	THF	2°	1 h	(0)[a]	36
Br	Et	$FeCl_3$	0.00625	THF	rt	1 h	(0)[a]	36
ClO_2S	Ph	$Fe(acac)_3$	5	THF/NMP	80°	2 h[b]	(24)	61
ClO_2S	4-MeC_6H_4	$Fe(acac)_3$	5	THF/NMP	80°	2 h[b]	(29)	61

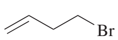
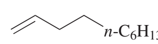
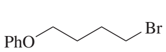
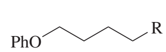
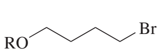
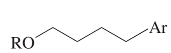
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	ZnI_2 + PhMgBr (2 eq)	$FeCl_3$ (1 mol %), TMEDA (1.2 eq), THF, 40°, 12 h	 (87)[c]	137
C_{3-4}				
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 R: $ClCH_2$ (86); OCN (90)	114, 41

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	PhMgBr	1. Catalyst (5 mol %), additives, THF, rt, 45 min (slow add.) 2. rt, 30 min		48

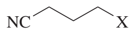
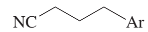
Catalyst	Additives	
$(FeCl_3)_2(tmeda)_3$	none	(75)
$Fe(acac)_3$	TMEDA (10 mol %), HMTA (5 mol %)	(75)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[b]	 (61)	61
	RMgBr	Catalyst (*x* mol %)		

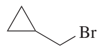
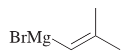
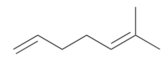
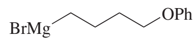
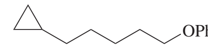
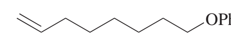
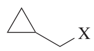
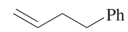
R	Catalyst	*x*	Solvent	Temp	Time (min)		Refs.
Et	$FeCl_3$	0.5	THF	2°	10	(0)[a]	5, 36
4-FC_6H_4	bmim•$FeCl_2$	0.1	Et_2O	—	10	(—)	133
4-MeC_6H_4	$Fe(acac)_3$	5	Et_2O	reflux	30	(—)	49

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	n-C_6H_{13}MgBr	$Fe(OAc)_2$ (3 mol %), XantPhos (6 mol %), Et_2O, rt, 15 min	 (46)[a]	135
	RMgBr	1. $FeCl_3$ (5 mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0°, 30 min	 R: CH_2=(TMS)C (58); CH_2=(Me)C (80); Me_2C=CH (91)	47
	ArMgBr	Catalyst (5 mol %)		

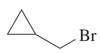
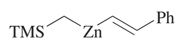
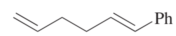
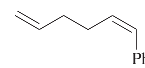
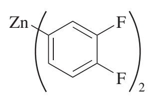
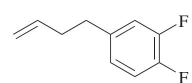
R	Ar	Catalyst	Solvent	Temp	Time (min)		Refs.
Ph	4-MeC_6H_4	$Fe(acac)_3$	Et_2O	reflux	30	(65)	49
2-BrC_6H_4	Ph	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	THF	–20°	5	(68)	41

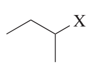
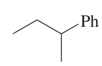
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	ArZnR	$FeCl_3$ (*x* mol %), additive, THF		

X	Ar	R	*x*	Additive	Temp (°)	Time (h)		Refs.
Br	3,4-$F_2C_6H_3$	3,4-$F_2C_6H_3$	3	dppbz (6 mol %)	80	12	(79)	138
I	4-$MeOC_6H_4$	4-$MeOC_6H_4$	5	TMEDA (1.5 eq)	50	0.5	(86)	138
I	4-$EtO_2CC_6H_4$	$TMSCH_2$	5	TMEDA (1.5 eq)	30	6	(72)	136

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $FeCl_3$ (10 mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0°, 30 min	 (—)	47
		$Fe(OAc)_2$ (3 mol %), XantPhos (6 mol %), Et_2O, rt, 15 min	 (46)[a] +  (2)[a]	135
	PhMgBr	Catalyst (5 mol %), ligand (*x* mol %)		

X	Catalyst	Ligand	*x*	Solvent	Temp (°)	Time (min)		Refs.
Br	$FeCl_3$	Et_3N	10	Et_2O/THF	45	30	(43)[a]	131
Br	$FeCl_3$	$P(c\text{-}C_6H_{11})_3$	10	Et_2O/THF	45	30	(54)[a]	46
Br	$FeCl_3$	P[O-2,4-(*t*-Bu)$_2C_6H_3$]$_3$	10	Et_2O/THF	45	30	(61)[a]	46
Br	$FeCl_3$	PEG (M_w = 14,000)	5	Et_2O	45	30	(62)	134
I	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	none	—	THF	–20	5	(100)[a]	41

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	 (*E*)/(*Z*) = 93:7	$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF, 30°, 6 h	 **I** +  **II** **I** + **II** (86), **I**/**II** = 90:10	56
		$FeCl_2(dppbz)_2$ (3 mol %), THF, 60°, 6 h	 (77)	138

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	1. Catalyst (5 mol %), additive, THF, time 1 (slow add.) 2. Time 2		

X	Catalyst	Additive	Temp (°)	Time 1 (min)	Time 2 (min)		Refs.
Cl	$FeCl_3$	TMEDA (1.2 eq)	40	20	10	(84)[a]	66
Cl	$Fe(acac)_3$	TMEDA (10 mol %), HMTA (5 mol %)	0	45	30	(—)	48
Br	$FeCl_3$	TMEDA (1.2 eq)	rt	20	10	(94)[a]	66
Br	$Fe(acac)_3$	none	0	45	30	(45)	48
Br	$Fe(acac)_3$	TMEDA (0.1 eq)	0	45	30	(60)	48
Br	$Fe(acac)_3$	TMEDA (0.5 eq)	0	45	30	(90)	48
Br	$Fe(acac)_3$	TMEDA (1.3 eq)	0	45	30	(90)	48
Br	$Fe(acac)_3$	HMTA (2.5 mol %)	0	45	30	(55)	48
Br	$Fe(acac)_3$	HMTA (5 mol %)	0	45	30	(80)	48
Br	$Fe(acac)_3$	TMEDA (10 mol %), HMTA (5 mol %)	0	45	30	(93)	48
Br	$(FeCl)_2(tmeda)_3$	none	0	45	30	(81)	48
I	$FeCl_3$	TMEDA (1.2 eq)	0	20	10	(95)[a]	66
I	$Fe(acac)_3$	TMEDA (10 mol %), HMTA (5 mol %)	0	45	30	(94)	48

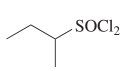
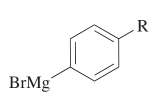
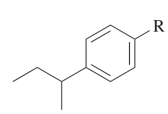
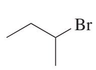
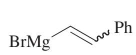
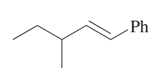
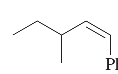
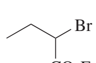
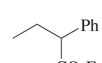
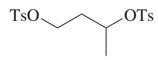
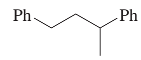
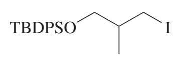
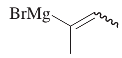
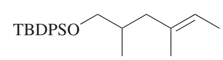
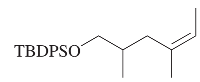
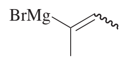
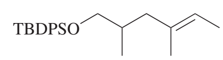
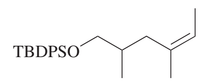
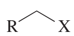
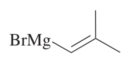
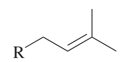
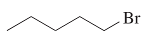
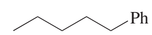
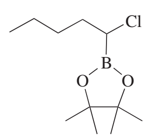
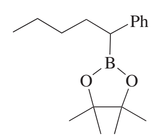
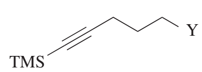
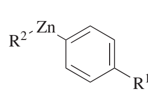
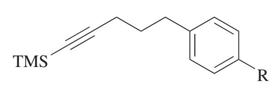
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[b]	 R: H (57); Me (75)	61
	 (*E*)/(*Z*) = 78:22	$Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.)	 **I** +  **II** **I** + **II** (68), **I**/**II** = 76:24	55
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, –20°, 5 min	 (87)	114, 41

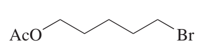
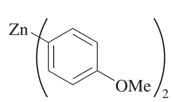
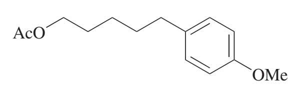
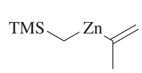
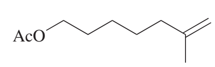
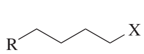
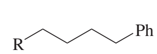
TABLE 12A. REACTION OF ALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	ZnI_2 + PhMgBr 2 eq	$FeCl_3$ (1 mol %), TMEDA (2.4 eq), THF, rt, 6 h	 (83)	137
	 (*E*)/(*Z*) = 70:30	Fe(acac)$_3$ (40 mol %), THF/NMP, 0° to rt, 2 h	 **I** +  **II**; **I** + **II** (—), **I/II** = —	47
	 (*E*)/(*Z*) = 70:30	$FeCl_3$ (10 mol %), TMEDA (1.9 eq), THF, 0°, 10 min; then rt, 30 min	 **I** +  **II**; **I** + **II** (70), **I/II** = —	47
C_{4-12}				
		1. $FeCl_3$ (*x* mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0°, 30 min		47

R	X	*x*	
TBDPSOCH$_2$(Me)CH	I	5	(80)
EtO$_2$C(CH$_2$)$_3$	Br	10	(98)
n-C$_{11}$H$_{23}$	Br	10	(88)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	PhMgBr	1. Fe(acac)$_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.) 2. 0°, 30 min	 (70)	48
	PhMgBr	[Li(tmeda)]$_2$[Fe(C$_2$H$_4$)$_4$] (5 mol %), THF, –20°, 5 min	 (92)	41
		$FeCl_3$ (*x* mol %), TMEDA (1.5 eq), THF		

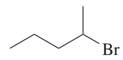
Y	R^1	R^2	*x*	Temp (°)	Time (h)		Refs.
I	H	Ph	5	50	0.5	(93)	136
I	EtO$_2$C	TMSCH$_2$	5	30	6	(91)	136
TsO	EtO$_2$C	TMSCH$_2$	1	rt	12	(75)	137

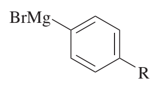
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (5 mol %), TMEDA (1.5 eq), THF, 50°, 0.5 h	 (83)	136
		$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF, 30°, 3 h	 (97)	56
C_{5-7}				
	PhMgBr	[Li(tmeda)]$_2$[Fe(C$_2$H$_4$)$_4$] (5 mol %), THF, –20°, 5 min		

R	X		Refs.
EtO$_2$C	Br	(88)	114
TBSO(CH$_2$)$_2$	I	(84)	41
NC(CH$_2$)$_2$	I	(83)	114, 41

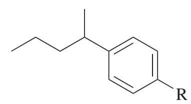
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.

C_5



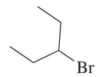


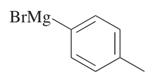
1. Catalyst (5 mol %), additive, THF, 45 min (slow add.)
2. 30 min



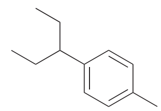
Refs. 48

R	Catalyst	Additive	Temp	
Me_2N	$Fe(acac)_3$	TMEDA (10 mol %), HMTA (5 mol %)	0°	(88)
MeO	$(FeCl_3)_2(tmeda)_3$	TMEDA (1.2 eq)	rt	(92)
MeO	$Fe(acac)_3$	TMEDA (10 mol %), HMTA (5 mol %)	0°	(93)

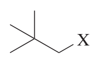




Catalyst (x mol %), ligand (y mol %), Et_2O, reflux, 30 min

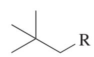


Catalyst	x	Ligand	y		Refs.
$FeCl_3$	5	Et_3N	10	(66)[a]	131
$FeCl_3$	5	TMEDA	5	(49)[a]	131
$FeCl_3$	5	DABCO	5	(40)[a]	131
$FeCl_3$	5	$P(c\text{-}C_6H_{11})_3$	10	(41)[c]	46
$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	(47)[c]	46
$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	(38)[c]	46
$FeCl_3$	5	PEG (M_w = 14,000)	5	(81)[c]	134
9	2.5	none	—	(56)[c]	132

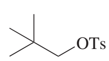


RMgBr

Catalyst (x mol %), THF

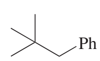


X	R	Catalyst	x	Temp	Time (min)		Refs.
Br	Et	$FeCl_3$	5	rt	20	(0)	36
Br	Et	$FeCl_3$	0.025	rt	45	(0)	36
I	Ph	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	5	–20°	5	(74)	114, 41



PhM

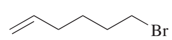
$FeCl_3$ (1 mol %), TMEDA (1.2 eq), additive (x mol %), THF, 50°, 12 h



M	Additive	x	
Li	$MgBr_2$	20	(5)[c]
MgBr	none	—	(19)

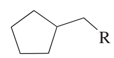
Refs. 137

C_6



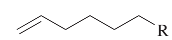
RMgBr

Catalyst (x mol %), ligand (y mol %)



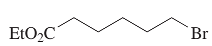
I

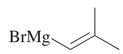
+



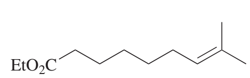
II

R	Catalyst	x	Ligand	y	Solvent	Temp	Time (h)	**I**	**II**	Refs.
Ph	$FeCl_3$	5	Et_3N	10	Et_2O/THF	45°	0.5	(30)[c]	(22)[c]	131
Ph	$FeCl_3$	5	$P(c\text{-}C_6H_{11})_3$	10	Et_2O/THF	45°	0.5	(40)[c]	(23)[c]	46
Ph	$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	Et_2O/THF	45°	0.5	(42)[c]	(25)[c]	46
Ph	$FeCl_3$	5	PEG (M_w = 14,000)	5	Et_2O	45°	0.5	(56)	(6)	134
$PhO(CH_2)_4$	$Fe(OAc)_2$	3	XantPhos	6	Et_2O	rt	0.25	(3)[a]	(48)[a]	135

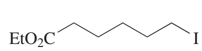


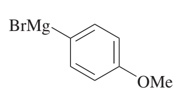


$Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.)

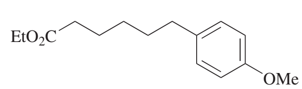


(73) 55

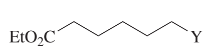




1. $FeCl_3$ (5 mol %), TMEDA (1.2 eq), THF, 0°, 20 min (slow add.)
2. 0°, 10 min

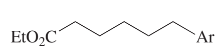


(88) 66



ArZnR

$FeCl_3$ (x mol %), TMEDA (y eq), THF



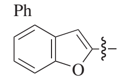
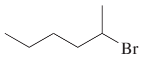
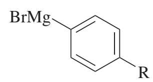
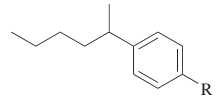
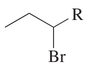
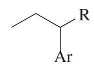
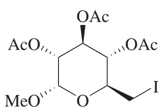
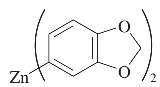
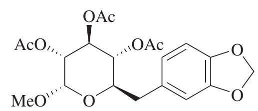
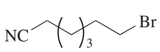
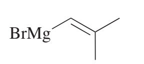
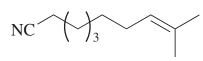
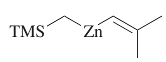
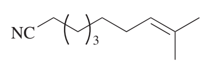
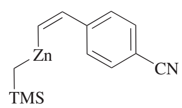
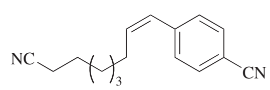
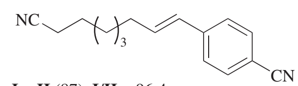
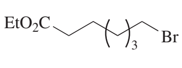
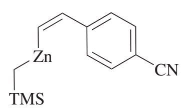
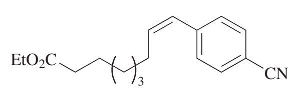
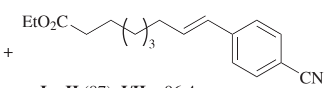
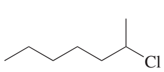
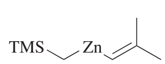
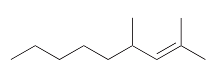
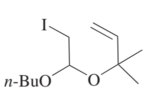
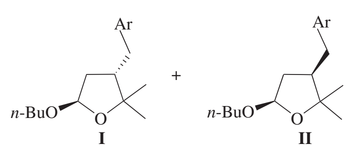
Y	Ar	R	x	y	Temp	Time (h)		Refs.
Br	Ph	Ph	5	1.5	50°	0.5	(91)	136
I	Ph	Ph	5	1.5	50°	0.5	(99)	136
TsO	Ph	Ph	1	1.2	rt	3	(95)	137
I		$TMSCH_2$	5	1.5	30°	6	(89)	136

TABLE 12A. REACTION OF ALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

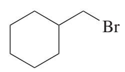
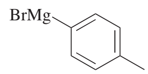
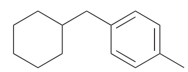
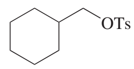
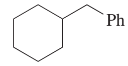
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		1. $Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.) 2. 0°, 30 min	 R: Me_2N (67); MeO (88)	48
$C_{6–7}$				
	ArMgBr	1. Catalyst (5 mol %), additive (*x* mol %), THF, 45 min (slow add.) 2. 30 min		48

R	Ar	Catalyst	Additive	*x*	Temp	
n-C_3H_7	Ph	$Fe(acac)_3$	TMEDA, HMTA	10, 5	0°	(71)
n-C_3H_7	4-$Me_2NC_6H_4$	$Fe(acac)_3$	TMEDA, HMTA	10, 5	0°	(85)
n-C_3H_7	4-$MeOC_6H_4$	$(FeCl_3)_2$(tmeda)$_3$	none	—	rt	(83)
n-C_4H_9	4-$MeOC_6H_4$	$Fe(acac)_3$	TMEDA, HMTA	10, 5	0°	(74)

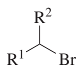
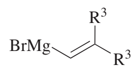
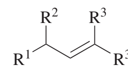
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		$FeCl_3$ (5 mol %), TMEDA (2.0 eq), THF, 50°, 0.5 h	 (90)	136
C_7				
		1. $Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.) 2. 0°, 30 min	 (67)	55
		$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF, 30°, 3 h; then 40°, 6 h	 (95)	56
	 (*Z*)/(*E*) = 96:4	$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF, 30°, 3 h; then 40°, 6 h	 **I** +  **II** **I** + **II** (87), **I**/**II** = 96:4	56
	 (*Z*)/(*E*) = 96:4	$FeCl_3$ (5 mol %), TMEDA (5 eq), THF, 30°, 6 h	 **I** +  **II** **I** + **II** (87), **I**/**II** = 96:4	56
		$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF, 30°, 18 h	 (91)[c]	56
	ArZnR	$FeCl_3$ (5 mol %), additive, THF		

Ar	R	Additive	Temp (°)	Time (h)	**I + II**	**I/II**	
Ph	Ph	TMEDA (1.5 eq)	50	0.5	(76)	63:37	136
3,4-$F_2C_6H_3$	$TMSCH_2$	dppbz (6 mol %)	60	15	(85)	61:39	138
3,4-$OCH_2OC_6H_3$	3,4-$OCH_2OC_6H_3$	TMEDA (1.5 eq)	50	0.5	(86)	64:36	136
4-NCC_6H_4	$TMSCH_2$	TMEDA (1.5 eq)	30	24	(73)	63:37	136

TABLE 12A. REACTION OF ALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		bmim-$FeCl_4$ (10 mol %), Et_2O, 0°, 10 min	 (64)	133
	ZnI_2 + PhM (2 eq)	$FeCl_3$ (1 mol %), TMEDA (1.2 eq), additive (*x* mol %), THF, rt		137

M	Additive	*x*	Time (h)	
Li	$MgBr_2$	20	12	(86)[c]
MgBr	none	—	24	(95)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-10}				
		$Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.)		55

R^1	R^2	R^3	
n-C_7H_{15}	H	Me	(69)
n-C_6H_{13}	Me	H	(55)
n-C_6H_{13}	Me	Me	(72)
n-C_9H_{19}	H	H	(48)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
n-$C_8H_{17}X$	PhMgBr	$FeCl_3$ (5 mol %), TMEDA (1.2 eq), THF, 20 min (slow add.); then 10 min	n-$C_8H_{17}Ph$	66

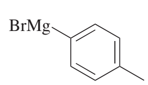
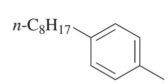
X	Temp	
Cl	40°	(45)[a]
Br	rt	(91)[a]
I	0°	(97)[a]

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
n-$C_8H_{17}SO_2Cl$	RMgX	$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[b]	n-$C_8H_{17}R$	61

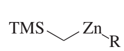
R	X	
Ph	Br	(72)
4-$MeOC_6H_4$	Br	(82)
$Ph(CH_2)_2$	Cl	(6)
4-MeC_6H_4	Br	(68)
1-Np	Br	(—)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
n-$C_8H_{17}Y$	RMgBr	$Fe(acac)_3$ (5 mol %), Et_2O, reflux, 0.5 h	n-$C_8H_{17}R$	49

Y	R	
Br	4-FC_6H_4	(60)
Br	2-MeC_6H_4	(62)
Br	4-$MeOC_6H_4$	(73)
Br	2,4,6-$Me_3C_6H_2$	(60)
Cl	4-MeC_6H_4	(32)
Br	4-MeC_6H_4	(70)
I	4-MeC_6H_4	(60)
TsO	4-MeC_6H_4	(50)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
n-$C_8H_{17}Br$		Catalyst (*x* mol %), ligand (*y* mol %), Et_2O, 0.5 h		

Catalyst	*x*	Ligand	*y*	Temp		Refs.
$FeCl_3$	5	Et_3N	10	reflux	(70)[c]	131
$FeCl_3$	5	DABCO	5	reflux	(62)[c]	131
$FeCl_3$	5	TMEDA	5	reflux	(63)[c]	131
$FeCl_3$	5	$P(c$-$C_6H_{11})_3$	10	reflux	(71)[c]	46
$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	reflux	(48)[c]	46
$FeCl_3$	5	P[O-2,4-(t-Bu)$_2C_6H_3$]$_3$	10	reflux	(58)[c]	46
$FeCl_3$	5	PEG (M_w = 14,000)	5	45°	(85)[c]	134
9	2.5	none	—	45°	(89)[c]	132
1	5	none	—	reflux	(71)	46

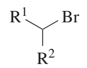
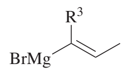
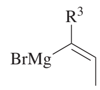
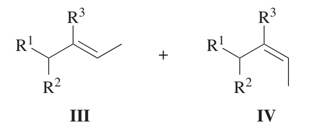
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
n-$C_8H_{17}OTs$		$FeCl_3$ (*x* mol %), TMEDA (*y* eq), THF	n-$C_8H_{17}R$	137

R	*x*	*y*	Temp (°)	Time (h)	
2-thienyl	3	3	40	12	(72)
3-thienyl	5	3	40	12	(72)
2-NCC_6H_4	5	3	40	14	(60)
3-NCC_6H_4	3	3	40	6	(93)
4-NCC_6H_4	1	1.5	rt	10	(93)

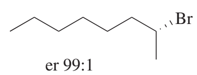
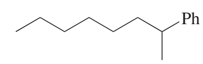
TABLE 12A. REACTION OF ALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

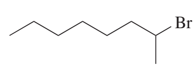
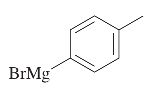
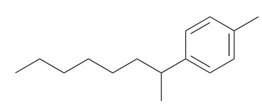
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
n-$C_8H_{17}OTs$	ZnX_2 + PhM (2 eq)	$FeCl_3$ (1 mol %), TMEDA (1.2 eq), additive (x mol %), THF, rt, 3 h	n-$C_8H_{17}Ph$	137

X	M	Additive	x	
Cl	MgBr	none	—	(12)[a]
I	MgBr	none	—	(88)[a]
I	MgBr	$TMSCH_2MgCl$	—	(87)[a]
I	Li	none	—	(0)[a]
I	Li	$MgBr_2$	20	(99)[a]

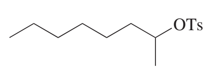
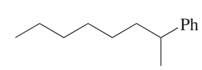
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-10}				
	 I +  II	$Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.)	 III + IV	55

R^1	R^2	R^3	**I/II**	**III + IV**	**III/IV**
n-C_6H_{13}	Me	H	86:14	(67)	85:15
n-C_6H_{13}	Me	H	97:3	(69)	97:3
n-C_9H_{19}	H	H	86:14	(67)	85:15
n-C_6H_{13}	Me	Me	87:13	(84)	85:15
n-C_9H_{19}	H	Me	86:14	(80)	86:14

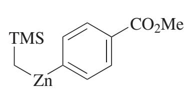
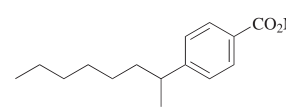
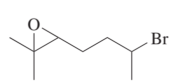
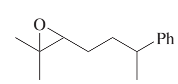
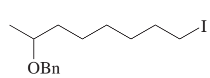
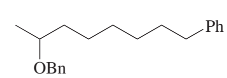
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
 er 99:1	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (93) er 50:50	114, 41

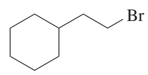
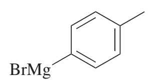
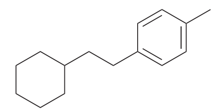
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (5 mol %), Et_2O		

Catalyst	Temp	Time (min)		Refs.
$Fe(acac)_3$	reflux	30	(73)	49
bmim-$FeCl_4$	0°	10	(84)	133

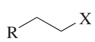
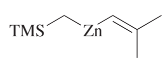
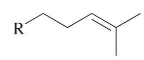
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	ZnI_2 + PhM (2 eq)	$FeCl_3$ (1 mol %), TMEDA (1.2 eq) additive (x mol %), THF, rt		137

M	Additive	x	Time (h)	
Li	$MgBr_2$	20	1	(86)[c]
MgBr	none	—	6	(90)

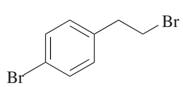
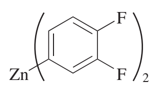
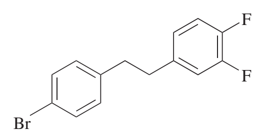
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (1 mol %), TMEDA (1.5 eq), THF, rt, 24 h	 (71)	137
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (66)	41
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (95)	114

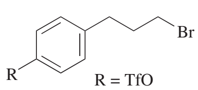
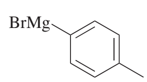
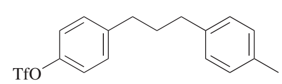
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		Catalyst (*x* mol %), ligand (*y* mol %), Et_2O		

Catalyst	*x*	Ligand	*y*	Temp	Time (h)		Refs.
$FeCl_3$	5	Et_3N	10	reflux	0.5	(74)[c]	131
$FeCl_3$	5	DABCO	5	reflux	0.5	(44)[c]	131
$FeCl_3$	5	TMEDA	5	reflux	0.5	(61)[c]	131
$FeCl_3$	5	$P(c\text{-}C_6H_{11})_3$	10	reflux	–	(64)[c]	46
$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	reflux	–	(64)[c]	46
$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	reflux	–	(65)[c]	46
$FeCl_3$	5	PEG (M_w = 14,000)	5	reflux	0.5	(91)[c]	134
9	2.5	none	—	45°	0.5	(69)[c]	132

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{8-10}				
		$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF		56

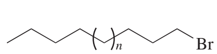
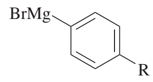
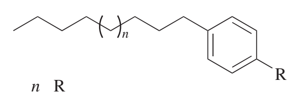
R	X	Temp (°)	Time (h)	
$4\text{-}BrC_6H_4$	Br	30	48	(73)
$n\text{-}C_8H_{17}$	Cl	50	24	(80)
$n\text{-}C_8H_{17}$	Br	40	18	(89)
$n\text{-}C_8H_{17}$	I	30	15	(98)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		$FeCl_2(dppbz)_2$ (3 mol %), THF, 60°, 15 h	 (90)[c]	138

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
 R = TfO		$Fe(acac)_3$ (5 mol %), Et_2O, reflux, 0.5 h	 (69)	49
C_{10}				
$n\text{-}C_{10}H_{21}Br$	RMgBr	Catalyst (*x* mol %), ligand (*y* mol %), Et_2O, rt, 15 min	$n\text{-}C_{10}H_{21}R$	135

R	Catalyst	*x*	Ligand	*y*	
n-Bu	$Fe(OAc)_2$	1	—	1	(3)[a]
n-Bu	$Fe(OAc)_2$	1	PPh_3	1	(15)[a]
n-Bu	$Fe(OAc)_2$	1	$P(c\text{-}C_6H_{11})_3$	1	(2)[a]
n-Bu	$Fe(OAc)_2$	1	2-(di-*t*-butylphosphino)biphenyl	1	(4)[a]
n-Bu	$Fe(OAc)_2$	1	2-(dicyclohexylphosphino)-2',6'-dimethoxybiphenyl	1	(8)[a]
n-Bu	$Fe(OAc)_2$	1	1,2-bis(dipentafluorophenylphosphino)ethane	1	(5)[a]
n-Bu	$Fe(OAc)_2$	1	dppe	1	(5)[a]
n-Bu	$Fe(OAc)_2$	1	BINAP	1	(18)[a]
n-Bu	$Fe(OAc)_2$	1	XantPhos	1	(51)[a]
n-Bu	$Fe(OAc)_2$	1	bis(2-diphenylphosphinophenyl)ether	1	(5)[a]
n-Bu	$Fe(OAc)_2$	1	9,9-dimethyl-4,5-bis(di-*t*-butylphosphino)xanthene	1	(11)[a]
n-Bu	$Fe(OAc)_2$	1	$P(n\text{-}Bu)_3$	1	(14)[a]
n-Bu	$Fe(OAc)_2$	1	$P(OCH_2CF_3)_3$	1	(2)[a]
n-Bu	$Fe(acac)_3$	1	XantPhos	1	(9)[a]
n-Bu	$FeCl_2$	1	XantPhos	1	(3)[a]
n-Bu	$FeCl_3$	1	XantPhos	1	(2)[a]
n-Bu	FeF_3	1	XantPhos	1	(15)[a]
n-Bu	$Fe(CF_3COCH{=}COMe)_3$	1	XantPhos	1	(3)[a]
n-Bu	$Fe(OAc)_2$	3	XantPhos	6	(64)[a]
$n\text{-}C_6H_{13}$	$Fe(OAc)_2$	3	XantPhos	6	(62)[a]

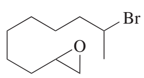
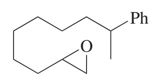
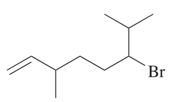
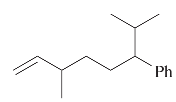
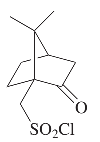
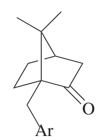
TABLE 12A. REACTION OF ALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10-12}				
		1. $Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.) 2. 0°, 30 min		48

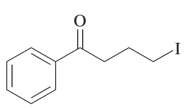
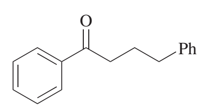
n	R	
3	H	(76)
3	MeO	(72)
5	MeO	(39)
5	Me	(50)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
n-$C_{10}H_{21}SO_2Cl$	PhMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[b]	n-$C_{10}H_{21}Ph$ (54)	61
n-$C_{10}H_{21}X$	ArZnR	$FeCl_3$ (x mol %), additive, THF	n-$C_{10}H_{21}Ar$	

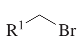
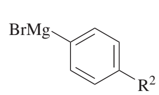
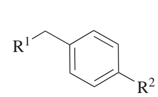
X	Ar	R	x	Additive	Temp (°)	Time (h)		Refs.
I	2-pyridyl	$TMSCH_2$	5	TMEDA (1.5 eq)	30	6	(98)	136
Cl	3,4-$F_2C_6H_3$	3,4-$F_2C_6H_3$	3	dppbz (6 mol %)	80	12	(—)	138
Br	3,4-$F_2C_6H_3$	3,4-$F_2C_6H_3$	3	dppbz (6 mol %)	80	12	(84)	138
I	3,4-$F_2C_6H_3$	3,4-$F_2C_6H_3$	3	dppbz (6 mol %)	80	6	(84)	138
I	2,3-F_2-4-$MeOC_6H_2$	2,3-F_2-4-$MeOC_6H_2$	3	dppbz (9 mol %)	60	24	(84)	138

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (56)	41
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (89)	114, 41
	ArMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[b]		61

Ar	
Ph	(34)
4-$MeOC_6H_4$	(42)
4-MeC_6H_4	(32)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (91)	114, 41
C_{11}				
n-$C_{11}H_{23}X$	ArMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	n-$C_{11}H_{23}Ar$	114

X	Ar	
Br	Ph	(61)
I	Ph	(96)
I	2,4-$Me_2C_6H_3$	(94)
I	3,4-$(MeO)_2C_6H_3$	(94)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11-12}				
		bmim-$FeCl_4$ (x mol %), Et_2O, 0°, 10 min		133

R^1	R^2	x	
1-Np	F	5	(60)
n-$C_{11}H_{23}$	F	0.1	(—)[a]
n-$C_{11}H_{23}$	F	0.5	(79)[a]
n-$C_{11}H_{23}$	F	1	(80)[a]
n-$C_{11}H_{23}$	F	5	(90)[a]
n-$C_{11}H_{23}$	F	10	(88)[a]
n-$C_{11}H_{23}$	Me	5	(73)
n-$C_{11}H_{23}$	Ph	5	(60)

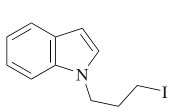
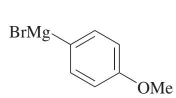
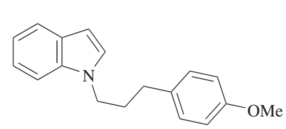
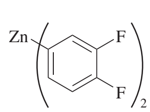
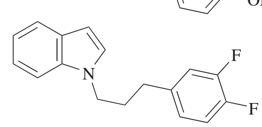
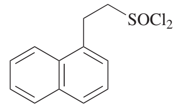
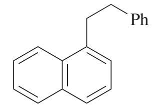
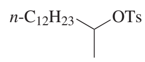
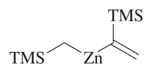
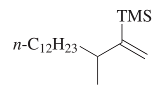
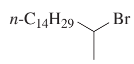
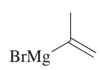
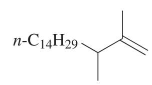
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
		1. $FeCl_3$ (5 mol %), TMEDA (1.2 eq), THF, 0°, 20 min (slow add.) 2. 0°, 10 min	 (87)	66
		$FeCl_3$ (3 mol %), dppbz (6 mol %), THF, 60°, 3 h	 (83)	138

TABLE 12A. REACTION OF ALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}				
n-$C_{12}H_{25}Br$	n-BuMgBr	$Fe(OAc)_2$ (3 mol %), XantPhos (6 mol %), Et_2O, rt, 15 min	n-$C_{16}H_{34}$ (63)[a]	135
	PhMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[b]	 (78)	61
C_{14}				
		$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF, 30°, 48 h	 (83)	56
n-$C_{14}H_{29}Br$	n-C_4H_9MgBr	$Fe(OAc)_2$ (3 mol %), XantPhos (6 mol %), Et_2O, rt, 15 min	n-$C_{18}H_{38}$ (63)[b]	135
C_{16}				
n-$C_{16}H_{33}Y$	RMgBr	Catalyst (x mol %), ligand (y mol %)	n-$C_{16}H_{33}R$	
		1. $FeCl_3$ (10 mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0°, 30 min	 (52)	47

Y	R	Catalyst	x	Ligand	y	Solvent	Temp	Time (h)		Refs.
Br	n-Bu	$Fe(OAc)_2$	3	XantPhos	6	Et_2O	rt	0.25	(64)[a]	135
ClO_2S	Ph	$Fe(acac)_3$	5	none	—	THF/NMP	80°	2[b]	(47)	61

[a] The yield was determined by GLC.

[b] The addition was carried out at 2 mL/h.

[c] The yield was determined by NMR spectroscopy.

TABLE 12B. REACTION OF CYCLOALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

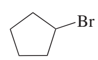
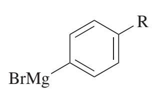
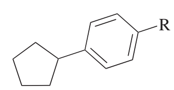
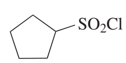
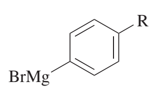
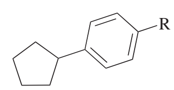
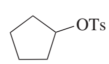
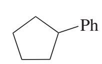
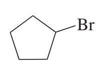
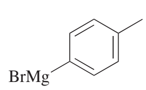
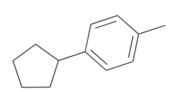
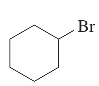
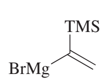
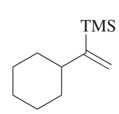
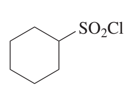
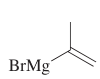
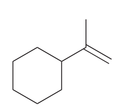
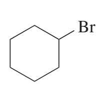
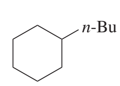
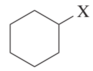
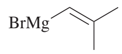
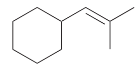
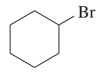
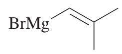
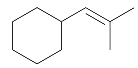
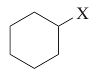
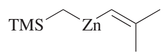
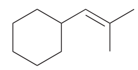
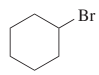
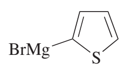
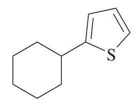
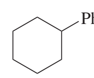
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to the charts preceding the tables for structures indicated by the **bold** numbers.*				
C_5				
		1. $Fe(acac)_3$ (5 mol %), TMEDA (10 mol%), HMTA (5 mol %), THF, 0°, 45 min (slow add.) 2. 0°, 30 min	 R: H (91); MeO (88)	48
		$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[c]	 R: H (63); Me (71)	61
	ZnI_2 + PhLi (2 eq)	$FeCl_3$ (1 mol %), TMEDA (1.2 eq), $MgBr_2$ (20 mol %), THF, rt, 1 h	 (91)[a]	137
		$FeCl_3$ (5 mol %), PEG (M_w = 14,000; 5 mol %), Et_2O, 45°, 0.5 h	 (78)[a]	134
C_6				
		1. $FeCl_3$ (5 mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0°, 0.5 h	 (—)	47
		$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[c]	 (48)	61
	n-BuMgBr	$Fe(OAc)_2$ (3 mol %), XantPhos (6 mol %), Et_2O, rt, 15 min	 (34)[b]	135

TABLE 12B. REACTION OF CYCLOALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		$Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 45 min (slow add.)	 X: Cl (15); I (74)	55
		1. Catalyst (5 mol %), THF, 0°, (slow add.) 2. 0°, 0.5 h		
		$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF		56
		$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (77)	41
	PhLi	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°		

Cyclohexyl bromide + BrMg-alkenyl:

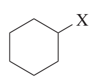
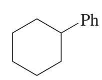
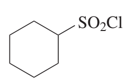
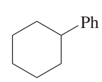
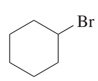
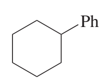
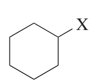
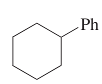
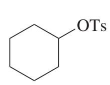
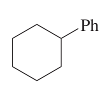
Catalyst	Additive	Time (h)		Refs.
$FeCl_3$	TMEDA (1.9 eq)	1	(64)[a]	47
$Fe(acac)_3$	TMEDA (10 mol %), HMTA (5 mol %)	0.75	(75)	55

Cyclohexyl-X + TMS-zinc reagent:

X	Temp (°)	Time (h)	
Cl	40	2	(91)[a]
Br	30	24	(99)[a]
I	30	18	(95)[a]

PhLi:

Time (min)		Refs.
5	(92)	114
—	(61)	41

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	1. $FeCl_3$ (5 mol %), TMEDA (1.2 eq), THF, 20 min (slow add.) 2. 10 min		66
	PhMgBr	$Fe(acac)_3$ (5 mol %), THF/NMP, 80°, 2 h[c]	 (68)	61
	PhMgBr	1. Catalyst (5 mol %), additive, THF, time 1 (slow add.) 2. Time 2		
	$ZnPh_2$	$FeCl_3$ (5 mol %), TMEDA (1.5 eq), THF, 50°		136
	ZnI_2 + PhM (2 eq)	$FeCl_3$ (1 mol %), TMEDA (1.2 eq), additive (*x* mol %), THF, rt		137

Cyclohexyl-X + PhMgBr:

X	Temp	
Cl	rt	(99)[a,b]
Br	0°	(99)[a,b]
I	0°	(99)[a,b]

Cyclohexyl bromide + PhMgBr:

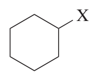
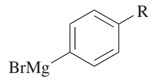
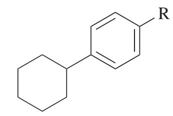
Catalyst	Additive	Temp	Time 1 (min)	Time 2 (min)		Refs.
$FeCl_3$	TMEDA (1.2 eq)	0°	20	10	(99)[a,b]	66
$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	none	–20°	—	5	(94)	114, 41
$[Li(dme)]_2[Fe(cod)_2]$	none	0° to rt	—	—	(87)	41
$[Li(tmeda)][CpFe(C_2H_4)_2]$	none	0° to rt	—	—	(81)	41
$Na_2Fe(CO)_4$	none	rt	—	—	(0)	41
$(FeCl_3)_2(tmeda)_3$	none	rt	45	30	(91)	48
$Fe(acac)_3$	TMEDA (10 mol %), HMTA (5 mol %)	0º	45	30	(90)[a]	48

Cyclohexyl-X + $ZnPh_2$:

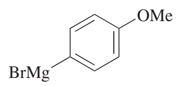
X	Time (h)	
Cl	3	(88)
Br	0.5	(97)
I	0.5	(98)

Cyclohexyl tosylate + ZnI_2 + PhM:

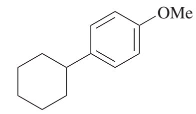
M	Additive	*x*	Time (h)	
Li	$MgBr_2$	20	12	(15)[a]
MgBr	none	—	24	(13)[a]

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		bmim-$FeCl_4$ (x mol %), Et_2O, 0°, 10 min		133

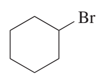
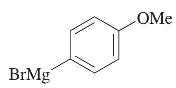
X	R	x	
Br	H	0.1	(20)[b]
Cl	Me	0.1	(75)
Br	Me	0.5	(89)
I	Me	1	(79)



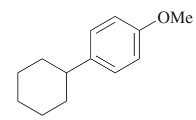
Catalyst (x mol %), ligand (y mol %)



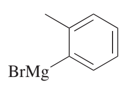
X	Catalyst	x	Ligand	y	Solvent	Temp	Time (min)		Refs.
Cl	$FeCl_3$	5	Et_3N	10	Et_2O	reflux	30	(84)	131
Cl	$FeCl_3$	5	TMEDA	5	Et_2O	reflux	30	(59)	131
Cl	$FeCl_3$	5	DABCO	5	Et_2O	reflux	30	(62)	131
Br	$FeCl_3$	5	$P(c\text{-}C_6H_{11})_3$	10	Et_2O	reflux	30	(76)[a]	46
Br	$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	Et_2O	reflux	30	(70)[a]	46
Br	$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	Et_2O	reflux	30	(88)[a]	46
Br	$FeCl_3$	5	PEG (M_w = 14,000)	5	Et_2O	45°	30	(78)[a]	134
Br	$FeCl_3$	5	PEG (M_w = 14,000), Hg (100–150 eq)	5	Et_2O	45°	30	(72)[a]	134
Br	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	5	none	—	THF	–20°	5	(95)	114, 41
Br	**9**	2.5	none	—	Et_2O	45°	30	(81)[b]	132

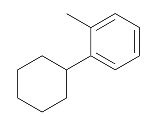
1. $FeCl_3$ (5 mol %), ligand, THF, time 1 (slow add.)
2. Time 2



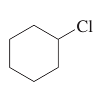
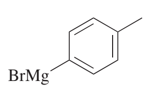
Ligand	Temp	Time 1 (min)	Time 2 (min)		Refs.
TMEDA (1.2 eq)	rt	20	10	(99)	66
TMEDA (10 mol %), HMTA (5 mol %)	0°	45	30	(89)	48



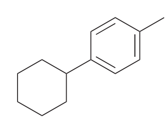
Catalyst (x mol %), ligand (y mol %),



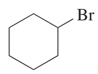
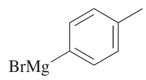
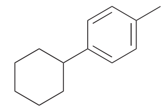
Catalyst	x	Ligand	y	Temp	Time (min)		Refs.
$FeCl_3$	5	TMEDA (1.2 eq)	—	rt	20[c]	(98)	66
$FeCl_3$	5	Et_3N	10	reflux	30	(75)[a]	131
$FeCl_3$	5	TMEDA	5	reflux	30	(62)[a]	131
$FeCl_3$	5	DABCO	5	reflux	30	(70)[a]	131
$FeCl_3$	5	$P(c\text{-}C_6H_{11})_3$	10	reflux	30	(44)[a]	46
$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	reflux	30	(60)[a]	46
$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	reflux	30	(31)[a]	46
$FeCl_3$	5	PEG (M_w = 14,000)	5	45°	30	(30)[a]	134
9	2.5	none	—	45°	30	(61)[b]	132

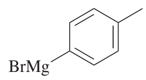
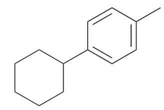
Catalyst (x mol %), ligand (y mol %), Et_2O, 0.5 h



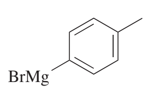
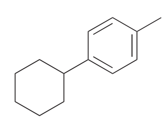
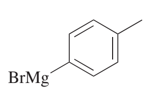
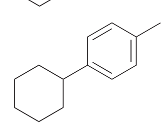
Catalyst	x	Ligand	y	Temp		Refs.
$FeCl_3$	5	Et_3N	10	reflux	(69)[a]	131
$FeCl_3$	5	TMEDA	5	reflux	(60)[a]	131
$FeCl_3$	5	DABCO	5	reflux	(74)[a]	131
$FeCl_3$	5	$P(c\text{-}C_6H_{11})_3$	10	reflux	(63)[a]	46
$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	reflux	(66)[a]	46
$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	reflux	(58)[a]	46
$FeCl_3$	5	**2**	—	reflux	(73)	46
$FeCl_3$	5	PEG (M_w = 14,000)	12.5	45°	(77)[a]	134
9	2.5	none	—	reflux	(80)[a]	132

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		Catalyst (5 mol %), ligand (*x* eq)		

Catalyst	Ligand	*x*	Solvent	Temp	Time (min)		Refs.
$Fe(acac)_3$	none	—	Et_2O	reflux	30	(69)	49
$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	none	—	THF	–20°	5	(81)	41
$FeCl_3$	TMEDA	1.2	THF	rt	20 (slow add.)	(96)	66

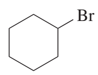
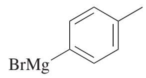
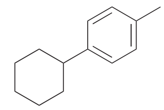
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (5 mol %), ligand (*x* mol %), Et_2O, reflux, 0.5 h		

Ligand	*x*		Refs.
Et_3N	10	(79)[a]	131
TMEDA	5	(79)[a]	131
DABCO	5	(88)[a]	131
PPh_3	20	(72)[b]	46
$P(c\text{-}C_6H_{11})_3$	10	(85)[b]	46
$P(c\text{-}C_6H_{11})_3$	20	(87)[b]	46
$P(2\text{-}MeC_6H_4)_3$	20	(53)[b]	46
$P(t\text{-}Bu)_2$(*o*-biphenyl)	20	(35)[b]	46
$P(c\text{-}C_6H_{11})_2$(*o*-biphenyl)	20	(27)[b]	46
$P(OMe)_3$	20	(83)[b]	46
$P(OEt)_3$	20	(69)[b]	46
$P(O\textit{i}\text{-}Pr)_3$	20	(83)[b]	46
$P(OPh)_3$	20	(67)[b]	46
$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	(88)[b]	46
$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	20	(82)[b]	46
$AsPh_3$	20	(82)[b]	46
dppm	10	(60)[b]	46
dppe	10	(66)[b]	46
dppp	10	(88)[b]	46
dppb	10	(75)[b]	46
$Ph_2P(CH_2)_5PPh_2$	10	(87)[b]	46
$Ph_2P(CH_2)_6PPh_2$	5	(85)[b]	46
$Ph_2P(CH_2)_6PPh_2$	10	(82)[b]	46
cis-dppen	10	(82)[b]	46
trans-dppen	10	(30)[b]	46
dppf	10	(60)[b]	46
$Ph_2AsCH_2AsPh_2$	10	(83)[b]	46
1	20	(87)[b]	46
2	20	(97)[b]	46
3	20	(45)[b]	46
4	20	(67)[b]	46
5	20	(94)[b]	46

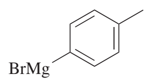
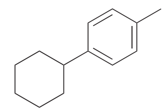
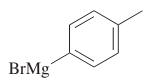
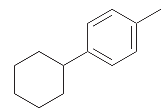
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_2$ (5 mol %), ligand (20 mol %), Et_2O, reflux, 0.5 h	 Ligand: PPh_3 (81)[b]; $P(c\text{-}C_6H_{11})_3$ (68)[b]	46
		$FeCl_3$ (5 mol %), ligand (*x* mol %), Et_2O, 0.5 h		134

Ligand	*x*	Temp	
PEG (M_w = 14,000)	0.5	reflux	(67)[a]
PEG (M_w = 14,000)	5	rt	(79)[a]
PEG (M_w = 14,000)	5	reflux	(94)[a]

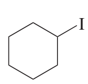
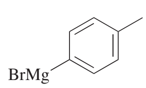
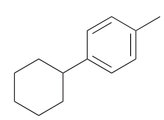
TABLE 12B. REACTION OF CYCLOALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
 *Continued from previous page.*		$FeCl_3$ (5 mol %), ligand (*x* mol %), Et_2O, 0.5 h		134

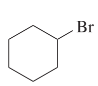
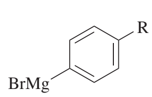
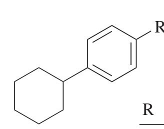
Ligand	*x*	Temp	
PEG (M_w = 14,000), Hg (100–150 eq)	5	reflux	(91)[a]
PEG (M_w = 14,000)	12.5	reflux	(80)[a]
PEG (M_w = 14,000)	50	reflux	(0)[a]
PEG (M_w = 14,000)	500	reflux	(0)[a]
PEG (M_w = 35,000)	5	reflux	(79)[a]
PEG (M_w = 2,000)	5	reflux	(63)[a]

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst **1** (5 mol %), Et_2O, reflux, 0.5 h	 (94)[b]	46
		Catalyst (*x* mol %), 45°, 0.5 h		132

Catalyst	*x*	Solvent	
2	0.1	Et_2O	(—)
2	0.5	Et_2O	(24)[b]
2	1	Et_2O	(52)[b]
2	2	Et_2O	(68)[b]
3	1	Et_2O	(11)[b]
4	1	Et_2O	(1)[b]
5	1	Et_2O	(9)[b]
6	1	Et_2O	(2)[b]
7	1	Et_2O	(—)
8	1	Et_2O	(51)[b]
9	1.5	Et_2O	(72)[b]
9	2.5	Et_2O	(90)[b]
9	2.5	THF/Et_2O	(84)[b]
10	1	Et_2O	(60)[b]

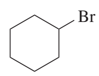
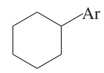
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), ligand (*y* mol %), Et_2O, 0.5 h		

Catalyst	*x*	Ligand	*y*	Temp		Refs.
$FeCl_3$	5	Et_3N	10	reflux	(75)[a]	131
$FeCl_3$	5	DABCO	5	reflux	(100)[a]	131
$FeCl_3$	5	TMEDA	10	reflux	(90)[a]	131
$FeCl_3$	5	$P(c\text{-}C_6H_{11})_3$	10	reflux	(75)[a]	46
$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	reflux	(85)[a]	46
$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	reflux	(81)[a]	46
$FeCl_3$	5	PEG (M_w = 14,000)	5	45°	(82)[a]	134
9	2.5	none	—	45°	(76)[a]	132

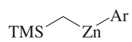
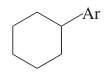
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$[Li(tmeda)]_2[Fe(C_2H_4)_4]$ (5 mol %), THF, 5 min		

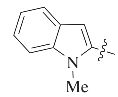
R	Temp (°)		Refs.
Cl	0	(67)	114, 41
$(TMS)_2N$	0	(88)	114
Me_2N	–20	(86)	41
Ph	0	(93)	114, 41

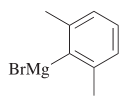
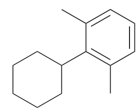
TABLE 12B. REACTION OF CYCLOALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	ArMgBr	1. $FeCl_3$ (5 mol %), TMEDA (1.2 eq), THF, 20 min (slow add.) 2. 10 min		66

Ar	Temp	
4-$CF_3C_6H_4$	0°	(67)
1-Np	rt	(97)[a]
2-Np	rt	(96)[a]

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (5 mol %), TMEDA (1.5 eq), THF		136

Ar	Temp	Time (h)	
4-NCC_6H_4	30°	6	(90)
	reflux	120	(78)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Catalyst (*x* mol %), ligand (*y* mol %), Et_2O, 0.5 h	 (—)	

Catalyst	*x*	Ligand	*y*	Temp	Refs.
$FeCl_3$	5	Et_3N	10	reflux	131
$FeCl_3$	5	DABCO	5	reflux	131
$FeCl_3$	5	TMEDA	10	reflux	131
$FeCl_3$	5	$P(c\text{-}C_6H_{11})_3$	10	reflux	46
$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	reflux	46
$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	reflux	46
$FeCl_3$	5	PEG (M_w = 14,000)	5	45°	134
9	2.5	none	—	45°	132

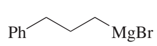
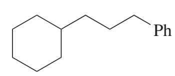
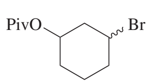
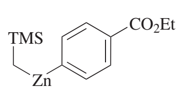
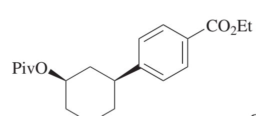
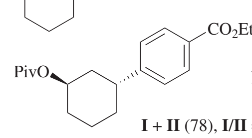
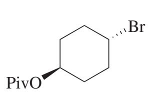
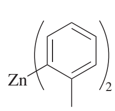
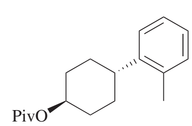
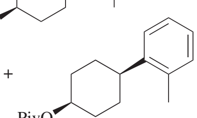
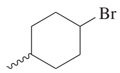
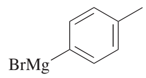
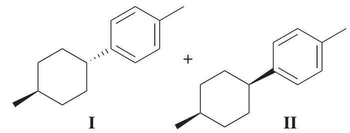
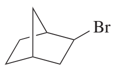
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Fe(OAc)_2$ (3 mol %), XantPhos (6 mol %), Et_2O, rt, 15 min	 (43)[b]	135
 *cis*/*trans* = 67:33		$FeCl_3$ (5 mol %), TMEDA (1.5 eq), THF, 30°, 6 h	 **I** +  **II** **I** + **II** (78), **I**/**II** = 53:47	136
		$FeCl_3$ (5 mol %), TMEDA (1.5 eq), THF, 50°, 0.5 h	 **I** +  **II** **I** + **II** (98), **I**/**II** = 55:45	136

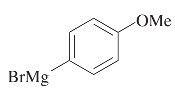
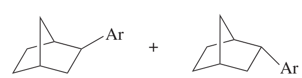
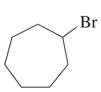
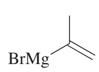
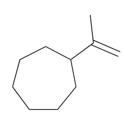
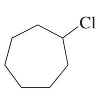
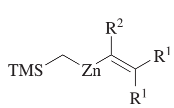
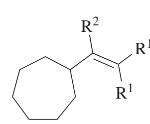
TABLE 12B. REACTION OF CYCLOALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Catalyst (x mol %), ligand (y mol %), Et_2O, 0.5 h	 **I** + **II**	

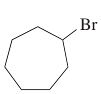
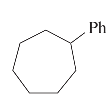
trans/cis	Catalyst	x	Ligand	y	Temp	**I + II**	**I/II**	Refs.
—	none	—	**2**	20	45°	(81)	69:31	46
76:24	$FeCl_3$	5	Et_3N	10	reflux	(85)[a]	60:40	131
76:24	$FeCl_3$	5	DABCO	5	reflux	(93)[a]	66:34	131
76:24	$FeCl_3$	5	TMEDA	10	reflux	(75)[a]	64:36	131
—	$FeCl_3$	5	$P(C\text{-}C_6H_{11})_3$	10	reflux	(72)[a]	68:32	46
—	$FeCl_3$	5	$P[O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_3]_3$	10	reflux	(70)[a]	67:33	46
—	$FeCl_3$	5	$Ph_2P(CH_2)_6PPh_2$	5	reflux	(70)[a]	67:33	46
—	$FeCl_3$	5	**6a**	5	reflux	(73)	71:29	134
—	$FeCl_3$	5	**6b**	5	reflux	(84)	70:30	134
—	$FeCl_3$	5	PEG (M_w = 14,000)	5	45°	(91)[a]	70:30	134
76:24	**9**	2.5	none	—	45°	(83)[a]	64:36	132
—	**1**	5	none	—	reflux	(89)	61:39	46
—	**11**	5	none	—	reflux	(55)	78:22	134
—	**12**	5	none	—	reflux	(44)	74:26	134

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RMgBr	Catalyst (x mol %), additive (y mol %)	 **I** + **II**	

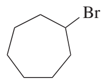
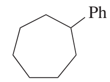
R	Catalyst	x	Additive	y	Solvent	Temp	Time (min)	**I + II**	**I/II**	Refs.
n-Bu	$Fe(OAc)_2$	3	XantPhos	6	Et_2O	rt	15	(8)[b]	**I** only	135
Ph	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	5	none	—	THF	–20°	5	(91)	94:6	41

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $FeCl_3$ (5 mol %), TMEDA (1.2 eq), THF, 0°, 20 min (slow add.) 2. 0°, 10 min	 **I** Ar = 4-$MeOC_6H_4$ **II** **I + II** (91)[a], **I/II** = 95:5	66
		1. $FeCl_3$ (10 mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.) 2. 0°, 0.5 h	 (94)[a]	47
		$FeCl_3$ (5 mol %), TMEDA (3.5 eq), THF		56

R^1	R^2	Temp (°)	Time (h)	
H	TMS	40	24	(79)
Me	H	30	18	(96)[a]

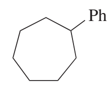
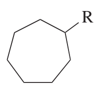
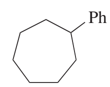
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	Catalyst (5 mol %), ligand, THF, –78 to 0°, 0.5 h		66

Catalyst	Ligand	
$FeCl_3$	none	(5)[b]
$FeCl_3$	*N*-methylmorpholine (1.2 eq)	(8)[b]
$FeCl_3$	Et_3N (1.2 eq)	(3)[b]

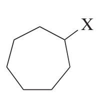
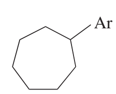
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	PhMgBr	Catalyst (5 mol %), ligand, THF, –78 to 0°, 0.5 h		66

Continued from previous page.

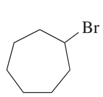
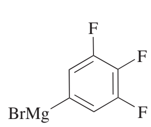
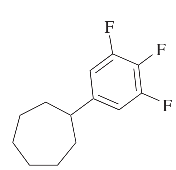
Catalyst	Ligand	
$FeCl_3$	NMP (1.2 eq)	(15)[b]
$FeCl_3$	DABCO (1.2 eq)	(20)[b]
$FeCl_3$	TMEDA (1.2 eq)	(71)[b]
$FeCl_3$	TEEDA (1.2 eq)	(23)[b]
$FeCl_3$	PPh_3 (10 mol %)	(6)[b]
$FeCl_3$	dppe (5 mol %)	(4)[b]
FeF_3	TMEDA (1.2 eq)	(—)[b]
$Fe(acac)_3$	TMEDA (1.2 eq)	(14)[b]
$FeCl_2$	TMEDA (1.2 eq)	(32)[b]
$Fe(CO)_5$	TMEDA (1.2 eq)	(—)[b]

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhMgBr	1. $FeCl_3$ (5 mol %), TMEDA (1.2 eq), THF, 0°, 20 min (slow add.) 2. 0°, 10 min	 (96)[b]	66
	See table.	$FeCl_3$ (*x* mol %), TMEDA (*y* eq), additive		

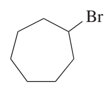
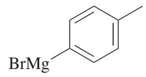
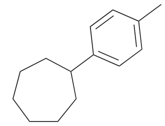
R	Nucleophile	*x*	*y*	Additive	Solvent	Temp	Time (h)		Refs.
Br	PhZnBr	5	1.5	none	THF	50°	0.5	(—)[b]	136
Br	$ZnCl_2$/PhLi	5	1.5	none	THF/Bu_2O	50°	0.5	(—)[b]	136
Br	$ZnCl_2$/PhLi/$TMSCH_2MgCl$	5	1.5	none	THF/pentane/Bu_2O	50°	0.5	(92)[b]	136
Br	$ZnCl_2$/(2 eq) PhLi	5	1.5	none	THF/Bu_2O	50°	0.5	(—)[b]	136
Br	$ZnCl_2$/PhMgBr	5	1.5	none	THF	50°	0.5	(—)[b]	136
Br	$ZnCl_2$/(2 eq) PhMgBr	5	1.5	none	THF	50°	0.5	(96)[b]	136
Br	$ZnCl_2$/PhMgBr/$TMSCH_2MgCl$	5	1.5	none	THF/Et_2O/Bu_2O	50°	0	(95)[b]	136
TsO	ZnI_2/(2 eq) PhLi	1	1.2	MgBr (20 mol %)	THF	rt	1	(81)	137
TsO	ZnI_2/(2 eq) PhMgBr	1	1.2	none	THF	rt	1	(88)	137

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	RZnAr	Catalyst (3 mol %), additive (*x* mol %), THF		138

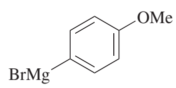
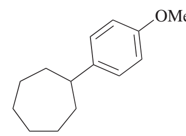
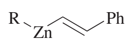
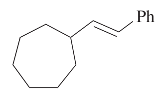
X	R	Ar	Catalyst	Additive	*x*	Temp (°)	Time (h)	
Br	4-FC_6H_4	4-FC_6H_4	$FeCl_3$	dppbz	6	60	3	(92)
Br	2,4-$F_2C_6H_3$	2,4-$F_2C_6H_3$	$FeCl_3$	dppbz	9	60	12	(79)
Cl	$TMSCH_2$	3,4-$F_2C_6H_3$	$FeCl_3$	dppbz	9	80	24	(83)
Br	3,4-$F_2C_6H_3$	3,4-$F_2C_6H_3$	$FeCl_3$	dppbz	6	60	3	(91)
Br	3,5-$F_2C_6H_3$	3,5-$F_2C_6H_3$	$FeCl_3$	dppbz	6	60	3	(84)[a]
Br	Cl	3,4,5-$F_3C_6H_2$	$FeCl_3$	dppbz	6	60	3	(18)[b]
Br	Cl	3,4,5-$F_3C_6H_2$	$FeCl_3$	dppbz	9	60	24	(86)[b]
Br	3,4,5-$F_3C_6H_2$	3,4,5-$F_3C_6H_2$	$FeCl_3$	none	—	60	3	(3)[b]
Br	3,4,5-$F_3C_6H_2$	3,4,5-$F_3C_6H_2$	$FeCl_3$	TMEDA	120	60	3	(—)[b]
Br	3,4,5-$F_3C_6H_2$	3,4,5-$F_3C_6H_2$	$FeCl_3$	dppbz	3	60	3	(72)[b]
Br	3,4,5-$F_3C_6H_2$	3,4,5-$F_3C_6H_2$	$FeCl_3$	dppbz	6	60	3	(91)[b]
Br	3,4,5-$F_3C_6H_2$	3,4,5-$F_3C_6H_2$	$FeCl_2(dppbz)_2$	none	—	60	3	(93)[b]

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$FeCl_3$ (3 mol %), ligand (*x* mol %), THF, 60°		138

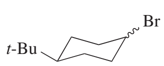
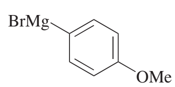
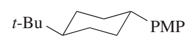
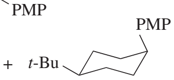
Ligand	*x*	
TMEDA	120	(1)[b]
dppbz	6	(7)[b]

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Catalyst (5 mol %), additive (*x* mol %)		

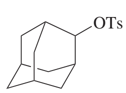
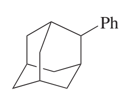
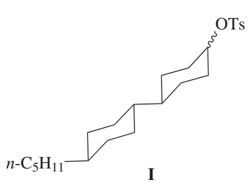
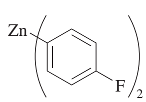
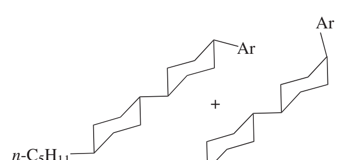
Catalyst	Additive	*x*	Solvent	Temp (°)	Time (min)		Refs.
$[Li(tmeda)]_2[Fe(C_2H_4)_4]$	none	—	THF	–20	5	(95)	114
$FeCl_3$	PEG (M_W = 14,000)	5	Et_2O	45	30	(79)	134

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $Fe(acac)_3$ (5 mol %), TMEDA (10 mol %), HMTA (5 mol %), THF, 0°, 0.75 h (slow add.) 2. 0°, 0.5 h	 (83)	48
		Catalyst (5 mol %), additive (*x* eq), THF		56

R	Catalyst	Additive	*x*	Temp (°)	Time (h)	
Br	$FeCl_3$	none	—	30	3	(8)[b]
$TMSCH_2$	$FeCl_3$	none	—	30	3	(25)[b]
$TMSCH_2$	$FeCl_3$	TMEDA	1.5	30	3	(56)[b]
$TMSCH_2$	$FeCl_3$	TMEDA	3.0	30	3	(91)[b]
$TMSCH_2$	$FeCl_3$	TMEDA	3.5	30	3	(95)[b]
$TMSCH_2$	$FeCl_3$	TMEDA	3.5	0	0.5[c]	(35)[b]
$TMSCH_2$	$FeCl_2$	TMEDA	3.5	30	3	(97)[b]
$TMSCH_2$	$Fe(acac)_3$	TMEDA	3.5	30	3	(85)[b]

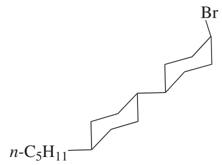
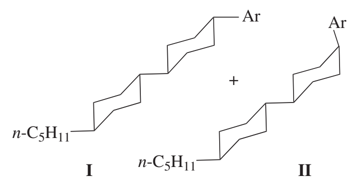
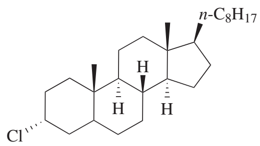
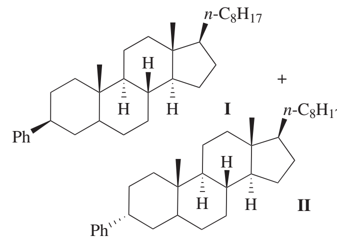
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
 **I**		1. $FeCl_3$ (5 mol %), TMEDA (1.2 eq), THF, 0°, 20 min (slow add.) 2. 0°, 10 min	 **II** +  **III**	66

I *cis/trans*	**II + III**	**II/III**
trans only	(96)	96:4
cis only	(98)[a]	4:96

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	ZnI_2 + PhMgBr (2 eq)	$FeCl_3$ (1 mol %), TMEDA (1.2 eq), THF, 40°, 12 h; then 60°, 6 h	 (57)	137
C_{17}				
 **I**		$FeCl_3$ (5 mol %), TMEDA (1.5 eq), THF, rt, 48 h; then 40°, 12 h	 **II** + **III** Ar = 4-FC_6H_4	137

I *cis/trans*	**II + III**	**II/III**
trans only	(60)	61:39
cis only	(—)	—

TABLE 12B. REACTION OF CYCLOALKYL ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}				
	Ar_2Zn	$FeCl_3$ (3 mol %), dppbz (9 mol %), THF, 60°, 24 h	 I + II Ar / I + II / I/II 3,4-$F_2C_6H_3$ / (85) / 56:44 3,4,5-$F_3C_6H_2$ / (69) / 56:44	137
C_{27}				
	Ph_2Zn	$FeCl_3$ (5 mol %), TMEDA (1.5 eq), THF, 50°, 12 h	 I + II **I + II** (89), **I/II** = 86:14	136

[a] The yield was determined by NMR spectroscopy.
[b] The yield was determined by GLC.
[c] The addition was carried out at 2 mL/h.

TABLE 13. REACTION OF HETEROCYCLIC ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS

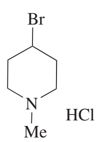
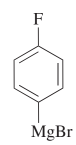
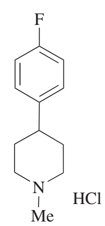
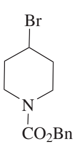
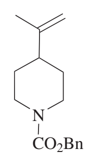
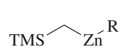
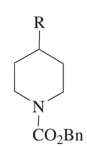
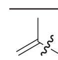
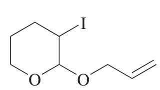
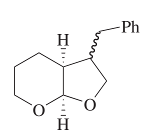
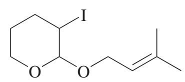
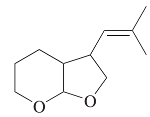
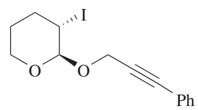
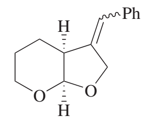
Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		bmim-$FeCl_4$ (5 mol %), Et_2O, 0°, 10 min	 (79)	133
		$FeCl_3$ (5 mol %), TMEDA (1.9 eq), THF, 0°, 1 h (slow add.); then 0°, 0.5 h	 (49)	61
		$FeCl_3$ (5 mol %), TMEDA (*x* eq), THF, 30°	 R / *x* / Time (h)  / 3.5 / 3 / (96)	56
			4-NCC_6H_4 / 1.5 / 24 / (79)	136
C_8				
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (85) dr 10:1	114, 41

TABLE 13. REACTION OF HETEROCYCLIC ELECTROPHILES WITH ORGANOMETALLIC COMPOUNDS (*Continued*)

Electrophile	Nucleophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (77)	114, 41
C_{14}				
	PhMgBr	$[Li(tmeda)]_2[Fe(C_2H_4)_4]$, (5 mol %), THF, –20°, 5 min	 (73) dr 10:1	41

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CHAPTER 2

THE BORONIC ACID MANNICH REACTION

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CONTENTS

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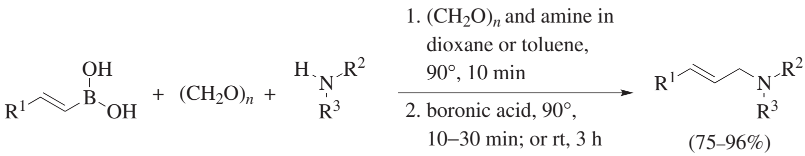
INTRODUCTION

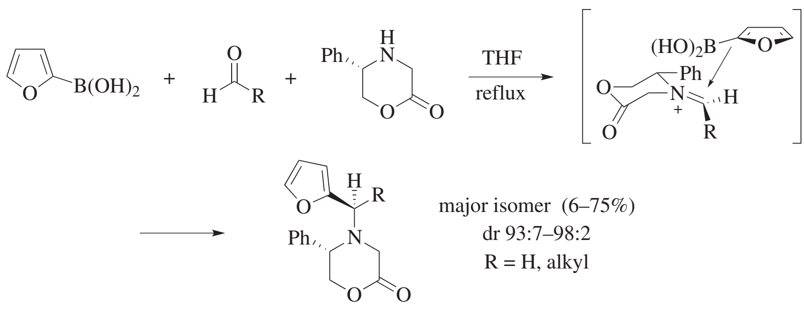
Multicomponent reactions (reactions involving three or more reagents, in a single flask, in which most of the atoms of each component are incorporated into the products) have been long established as powerful and economically efficient reactions.[1,2] Early examples of three-component reactions include the Mannich, Biginelli, Hantzsch, Strecker, and Passerini reactions.[1,2] The four-component Ugi

reaction is a relatively more recent addition.[1] The Mannich,[3] Biginelli,[4] Strecker,[5] and Passerini[6] reactions have been reviewed in earlier volumes of *Organic Reactions*. In 1993, Petasis reported the first boronic acid Mannich reaction between 1-alkenylboronic acids, secondary amines, and paraformaldehyde. These reactions afford tertiary allylic amine products in 75–96% yields (Eq. 1).[7] This reaction type has also been referred to as the Petasis reaction or the borono-Mannich reaction.



(Eq. 1)

In 1996 an asymmetric version was reported by Harwood et al. using the chiral cyclic amine (*S*)-5-phenyl-2-morpholinone, aldehydes, and 2-furanylboronic acid (Scheme 1).[8] Subsequently it was established that the boronic acid Mannich reaction could be extended to aryl-, alkenyl-, alkynyl-, and allylboronic acids, with ammonia, primary and secondary amines, mono-*N*-protected hydrazines, hydroxylamines, methoxyamines, and sulfinamides used as the amino component, but was generally limited to certain aldehydes and ketones (usually α-heteroatom-substituted). Those reactions involving chiral, enantioenriched components are often highly diastereoselective, making this three-component reaction extremely versatile for preparing important chiral starting materials for the synthesis of molecules of biological interest, including chiral α-amino acids, 1,2-amino alcohols, 2-aminoalkyl phenols, and alkaloids.



Scheme 1

The general and commercial availability of the three components of the boronic acid Mannich reaction makes it attractive to synthetic chemists. In particular, an increasing number of organoboronic acids and boronate esters and potassium organotrifluoroborate reagents are commercially available because of their use in other key transformations, such as the Suzuki–Miyaura reaction.[9] Importantly, these reagents are also readily prepared, are air and water stable, and are tolerant to many functional groups.[9]

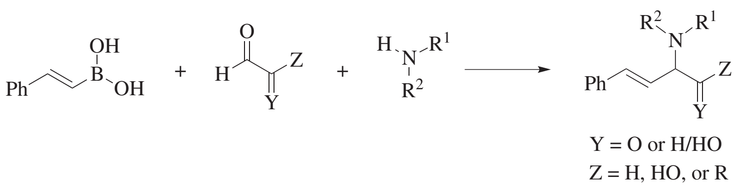
This chapter addresses the mechanism, stereochemistry, and the scope and limitations of each of the three components of the boronic acid Mannich reaction. Some typical experimental conditions are provided along with a comprehensive Tabular Survey in which reactions have been classified on the basis of the types of products that are formed.

The Tabular Survey includes the literature from the period 1993 to 2011. Supplemental references are provided in the bibliography for reactions reported in 2012 and in 2013 (up to the date of submission). Several other reviews on the boronic acid Mannich reaction have been published.[10–12]

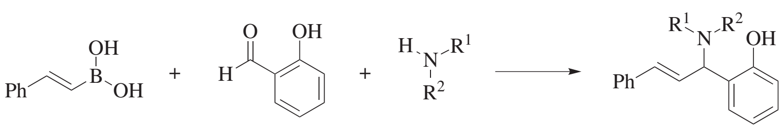
MECHANISM AND STEREOCHEMISTRY

Although the exact mechanism of the boronic acid Mannich reaction is not known, several mechanisms have been proposed that derive from the following observations:

(1) The boronic acid Mannich reaction works efficiently only with α-hetero-atom-substituted aldehydes (Z(C=Y)CHO) (Scheme 2) and 2-hydroxy aromatic aldehydes (salicylaldehydes) (Eq. 2).

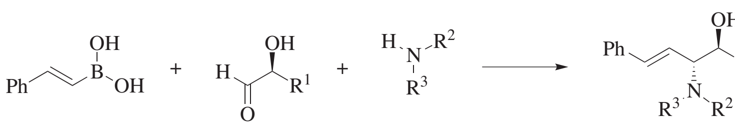


Scheme 2



(Eq. 2)

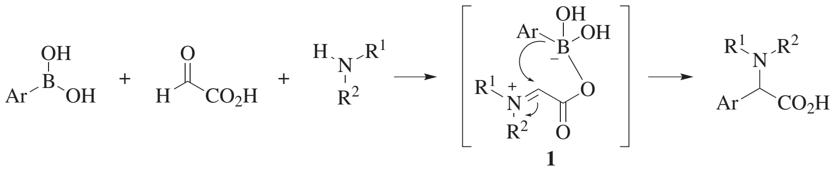
(2) When chiral α-hydroxy aldehydes are employed, *anti*-1,2-amino alcohol products are produced exclusively (Eq. 3).



(Eq. 3)

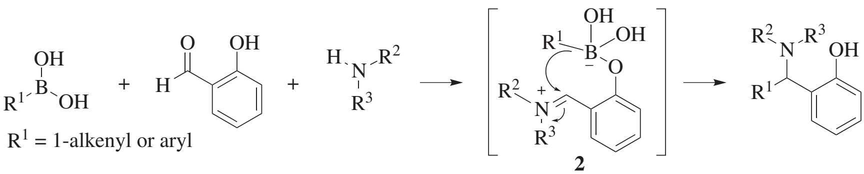
In 2000, a mechanism was suggested for the synthesis of α-phenylglycines from the reactions of arylboronic acids, glyoxylic acid, and secondary amines

(Scheme 3).[13] This process involves the iminium ion boronate zwitterionic intermediate **1** that allows for an efficient intramolecular delivery of the aryl substituent (Ar) of the boronic acid to the carbon of the reactive iminium ion moiety. The authors propose that the first step in the formation of intermediate **1** involves boronate ester formation between glyoxylic acid and the boronic acid followed by formation of the iminium ion.



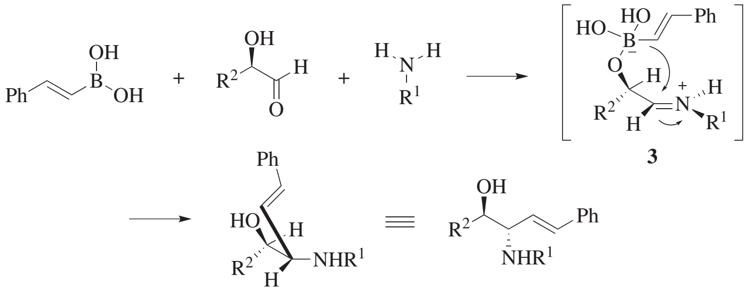
Scheme 3

In the following year, Petasis and Boral suggested a related mechanism involving the boronate intermediate **2** for the boronic acid Mannich reaction between salicylaldehyde, aryl- or 1-alkenylboronic acids, and secondary amines (Scheme 4).[14]



Scheme 4

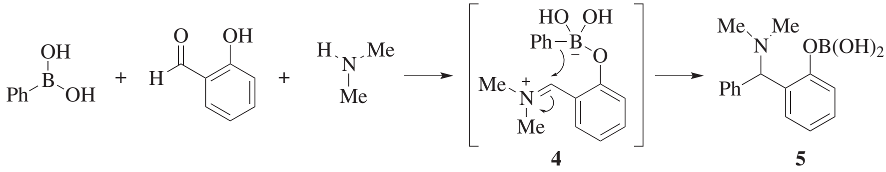
For reactions involving chiral α-hydroxy aldehydes, a boronate intermediate **3** has been proposed in which the iminium ion adopts the reactive conformation shown in Scheme 5 to minimize 1,3-allylic strain between the α-substituent and the NH of the iminium ion.[11,15]



Scheme 5

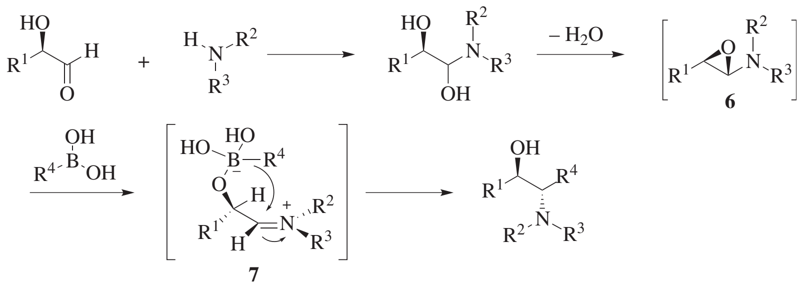
A theoretical study (using Density Functional Theory (DFT)) of the reaction between dimethylamine, phenylboronic acid, and salicylaldehyde in water

suggests an early transition structure between the iminium intermediate **4** and the amine product **5** (Scheme 6).[16] In the transition state structure, the phenyl group migrates from the boron atom to the carbon atom of the iminium ion with only incipient carbon–carbon bond formation identified.



Scheme 6

A DFT study on the mechanism of the reaction of *N*,*N*-dibenzylamine, styrenylboronic acid, and 2-hydroxypropanal in ethanol supports the intermediacy of boronate **3** (Scheme 5) in the irreversible carbon–carbon bond-forming reaction.[17] Interestingly, an epoxide precursor (**6**) to the iminium ion boronate intermediate **7** (compare with **3** in Scheme 5) is suggested instead of the α-hydroxyiminium ion (Scheme 7).



Scheme 7

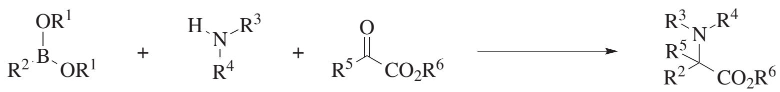
SCOPE AND LIMITATIONS

The accompanying comprehensive Tabular Survey in this chapter is organized into tables according to the structure of the product formed from the boronic acid Mannich reaction, which includes, but is not limited to, α-amino acids, 1,2-amino alcohols, benzylamines, and heterocycles. Accordingly, this part of the chapter, where the scope and limitations of each reaction partner will be discussed, is also organized into sections according to the structure of the product formed. Although the first example of the Petasis reaction was performed using formaldehyde as the carbonyl component (Eq. 1), the boronic acid Mannich reaction generally works efficiently only with α-heteroatom-substituted aldehydes and ketones. For example, glyoxylic acid (Scheme 3), salicylaldehydes (Scheme 4), and α-hydroxy aldehydes (Scheme 5) work efficiently to give α-amino acids, benzylamines, and 1,2-amino alcohols, respectively. Although ammonia, primary, and secondary

amines have been employed, secondary amines are generally more reactive, probably reflecting the more reactive nature of the initially formed iminium ion intermediate. Mono-*N*-protected hydrazines, hydroxylamines, methoxyamines, and sulfinamides have also been used as the amine component. The boronic acid component has been limited to boronic acid itself and those containing allyl, alkenyl, alkynyl, and aryl residues. In some cases the corresponding boronate esters or potassium trifluoroborates have been used instead. A variety of reaction media have been used, including aprotic (CH_2Cl_2, DCE, DMF, THF, dioxane, and MeCN) and protic solvents (water, MeOH, EtOH, 2,2,2-trifluoroethanol (TFE), and hexafluoroisopropyl alcohol (HFIP)), and combinations of both protic and aprotic solvents (e.g., HFIP/CH_2Cl_2). Often the use of HFIP gives superior yields. This outcome may be associated with the enhanced ability of this solvent to stabilize polar intermediates and transition state structures and/or the enhanced acidity of this solvent, providing general or specific acid catalysis. Reaction temperatures vary from ambient to 120° using conventional or microwave heating.

Preparation of α-Amino Acids and Derivatives

The boronic acid Mannich reactions of glyoxylic acid (**8**) and amines with aryl-, 1-alkenyl-, or allylboronic acids provide efficient syntheses of α-phenyl amino acids, α-vinyl amino acids (β-γ-unsaturated α-amino acids), and α-allyl amino acids, respectively (products **11** in Scheme 8 and Table 1). When ethyl glyoxylate **9** is employed, the corresponding α-amino ester derivatives **12** are formed (Table 2B). Clearly the mechanism proposed in Scheme 3 cannot operate in these cases. Perhaps the activating ester group sufficiently enhances the electrophilicity of the intermediate iminium ion to make intermolecular attack by the boronic acid (ester) more efficient. The use of mono-*N*-protected hydrazines, hydroxylamines, methoxyamines, and sulfinamides as nitrogen nucleophiles results in formation of the corresponding α-hydrazino, α-hydroxylamino, α-methoxyamino, and α-sulfinamido acids, respectively (Table 2A). Related reactions using 2-oxopropanoic acid (**10**, R^5 = Me, R^6 = H) rather than glyoxylic acid (**8**) as the carbonyl component give α-methyl α-substituted α-amino acids **13** or their derivatives (Table 2C). Polymer-supported examples that involve either the boronate ester, amine (Table 1), or aldehyde components anchored to the support have been



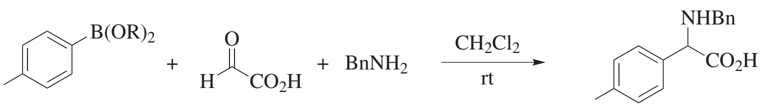
8	$R^5 = R^6 = H$	**11**
9	$R^5 = H, R^6 = Et$	**12**
10	R^5 = Me or Ph, R^6 = H or Me	**13**

R^1 = H, alkyl
R^2 = aryl, $R^8R^7C{=}CH–$, $R^{10}CH{=}CHCH(R^9)–$
R^3 = H, alkyl, aryl
R^4 = alkyl, R^{11}CONH (R^{11}CO = Boc, Cbz, H_2NCO), *t*-Bu(O)S

Scheme 8

reported (Table 2D). Methyl 2-oxopropanoate (**10**, $R^5 = R^6 = Me$) and methyl phenylglyoxylate (**10**, $R^5 = Ph$, $R^6 = Me$) react with allylic boronic acids and ammonia to give methyl α-allyl-α-methyl glycinates and α-allyl-α-phenyl glycinates, respectively (Table 2E).

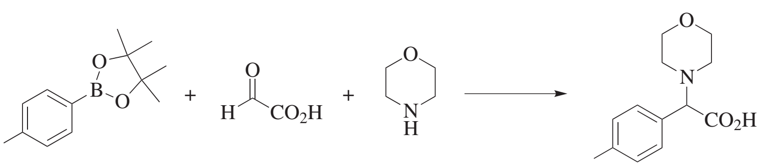
The Amine Component. Relatively unhindered primary amines are often poor reaction partners when arylboronic acids or boronates are used. For example, the attempted reaction of butylamine, glyoxylic acid, and phenylboronic acid in CH_2Cl_2/10% HFIP at room temperature for 45 hours gave only 7% conversion to the desired α-amino acid product.[18] Likewise, the reaction of benzylamine, glyoxylic acid, and the pinacol ester of 4-methylphenylboronic acid in CH_2Cl_2, or a variety of other solvents, is also unsuccessful (Scheme 9).[19] In contrast, the reaction of benzylamine, glyoxylic acid, and 4-methylphenylboronic acid under similar reaction conditions gives the desired amino acid in 67% yield (Scheme 9).[19] Ethyl glyoxylate reacts with 2-iodo- and 2-bromobenzylamine and electron-rich arylboronic acids to give the corresponding α-(*N*-2-halobenzylamino) esters.[20]



$(RO)_2$ = pinacol (0%)
R = H (67%)

Scheme 9

Secondary amines are in general more reactive; however, the choice of reaction solvent is often critical. For example, the reaction of morpholine, glyoxylic acid, and the pinacol ester of 4-methylphenylboronic acid in CH_2Cl_2 at room temperature affords the α-amino acid product but in only 12% yield.[19] Better yields are obtained using the protic solvents MeOH under microwave irradiation and HFIP at room temperature, as shown in Scheme 10.[21]

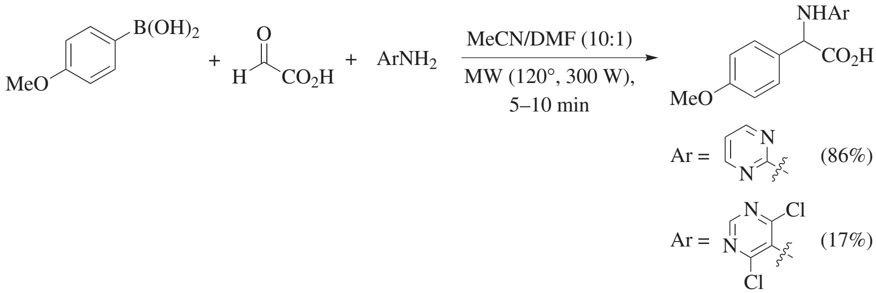


CH_2Cl_2, rt	(12%)
MeOH, MW (300 W), 120°, 10 min	(21%)
HFIP, rt, 4 h	(81%)

Scheme 10

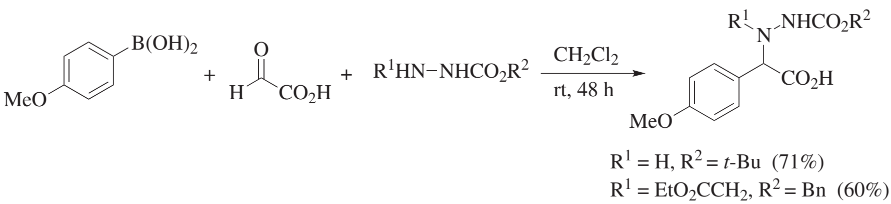
Unhindered ring-substituted anilines and 5- or 6-membered heteroaromatic amines react with aryl-, allyl-, and 1-alkenylboronic acids to provide the corresponding α-amino acids in good yields. Whereas the reaction of 2-aminopyrimidine, glyoxylic acid, and 4-methoxyphenylboronic acid gives the

expected α-amino acid in 86% yield, the yield of the corresponding α-amino acid is only 17% when the more hindered amine 4,6-dichloro-5-aminopyrimidine is used (Scheme 11).[22]



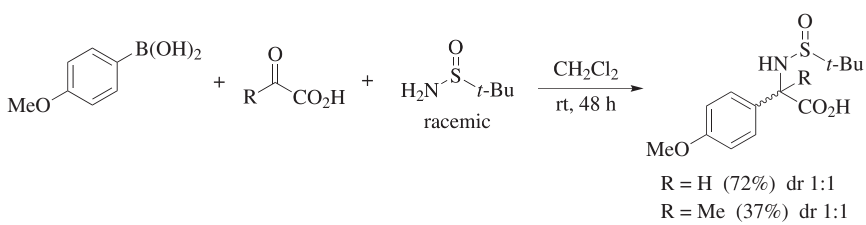
Scheme 11

α-Hydrazino acids are obtained when the amine component is a mono-*N*-Boc- or *N*-Cbz-protected hydrazine derivative.[23] For example, the reaction of 4-methoxyphenylboronic acid with glyoxylic acid and *tert*-butyl carbazate gives the corresponding α-hydrazino acid in 71% yield, and the same reaction using benzyl 2-(2-ethoxy-2-oxoethyl)hydrazinecarboxylate gives the corresponding α-hydrazino acid in 60% yield (Scheme 12).[23]



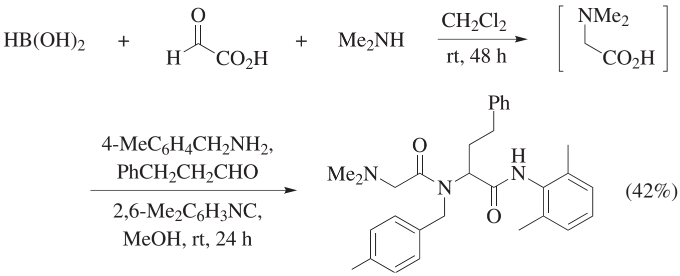
Scheme 12

The use of hydroxylamines, methoxyamines, and sulfinamides as the amino component results in the formation of the corresponding α-hydroxylamino, α-methoxyamino and α-sulfinamido acids (Table 2A). Racemic *tert*-butylsulfinamide gives a 1:1 mixture of diastereomeric α-sulfinamido acids in reactions with glyoxylic acid or 2-oxopropanoic acid and 4-methoxyphenylboronic acid (Scheme 13).[24] A similar lack of diastereoselectivity is observed with other boronic acids.[24]



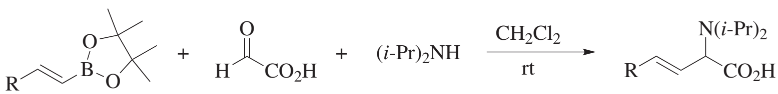
Scheme 13

The Organoboron Reagent Component. The reaction of boronic acid with dimethylamine and glyoxylic acid gives *N*,*N*-dimethylglycine,[25,26] which is not isolated but treated under Ugi reaction conditions to produce a diamide (Scheme 14).[25]



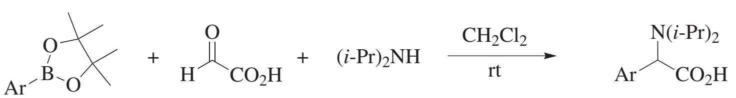
Scheme 14

Boronic acid Mannich reactions of glyoxylic acid with the secondary amines diisopropylamine, morpholine, or pyrrolidine and pinacol 1-alkenylboronate esters afford much higher product yields than their arylboronate ester counterparts under identical reaction conditions. Examples using diisopropylamine are shown in Schemes 15 and 16.[19]



R = Ph (75%)
R = 4-ClC$_6$H$_4$ (70%)

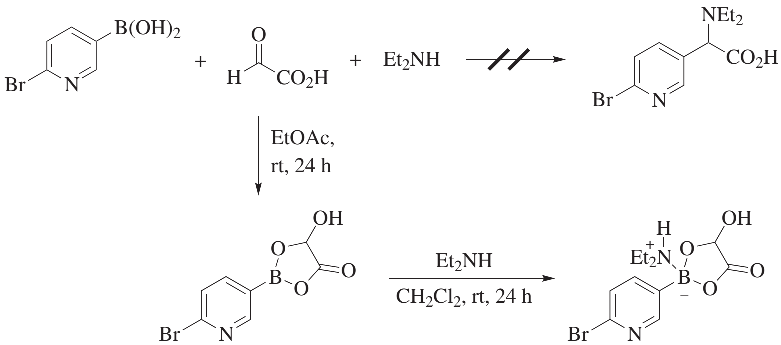
Scheme 15



Ar = 4-MeC$_6$H$_4$ (12%)
Ar = 4-BrC$_6$H$_4$ (6%)
Ar = 3-thienyl (27%)

Scheme 16

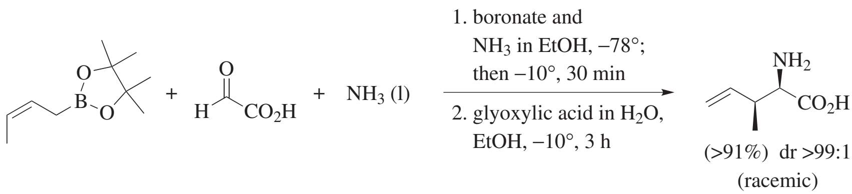
The majority of arylboronic acids and boronate esters that have been successfully employed in the synthesis of α-amino acids contain electron-rich arenes. The reaction between the relatively electron-poor 6-bromo-3-pyridylboronic acid, glyoxylic acid, and diethylamine results in formation of a precipitate that is not the desired α-pyridylglycine product but instead is the isolatable dioxaborolanone **14**, which is formed in 80% yield (Scheme 17).[27] This compound, when treated with diethylamine in CH_2Cl_2 at room temperature for 24 hours, affords the stable 1:1 complex **15** rather than the α-pyridylglycine derivative.



14 (80%) **15**

Scheme 17

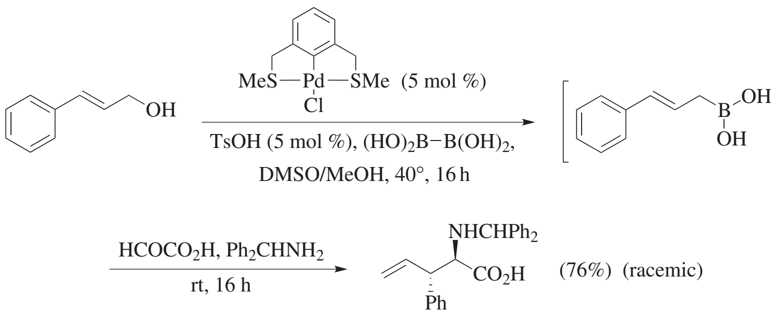
The pinacol ester of (Z)-2-butenylboronic acid reacts at the γ-carbon with glyoxylic acid and liquid ammonia in ethanol solution at $-10°$ to give a 2,3-*syn*-α-amino acid derivative with almost complete diastereoselectivity (Eq. 4).[28] High diastereoselectivities are also seen in the reactions of (Z)-2-butenylboronic acid and (E)-2-butenylboronic acid with ketones or α-keto esters and ammonia.[29]



(Eq. 4)

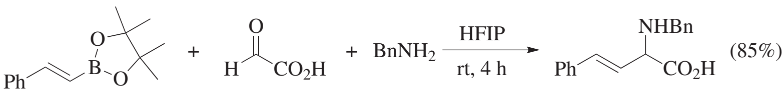
A method to generate (E)-allylboronates in situ from a palladium-catalyzed borylation reaction of allylic alcohols has been developed. After addition of glyoxylic acid and aniline, 4-methoxyaniline, or benzhydrylamine, the corresponding α-allylated amino acids are isolated in good overall yields for this one-pot process.[30] In a typical example (Scheme 18), cinnamyl alcohol undergoes a palladium-catalyzed borylation reaction, and the resulting allylic boronic acid is treated in the same pot with benzhydrylamine and glyoxylic acid at room temperature; addition at the γ-carbon of the allylic boronic acid provides the corresponding *anti*-α-allyl amino acid in 76% overall yield.

Solvent Effects. Studies of the effects of the solvent on the reaction between the pinacol ester of (E)-β-styrenylboronic acid, glyoxylic acid, and benzylamine have been reported from three different laboratories.[19,21,31] The aprotic solvents CH_2Cl_2,[19,21,31] toluene,[21] THF,[21] and dioxane[21] are not effective at room temperature. The combination of CH_2Cl_2 and an alcohol results in improved conversions, but the use of a pure alcohol solvent is the most effective, with the fluorinated alcohol solvents TFE and HFIP performing better than methanol. The use of



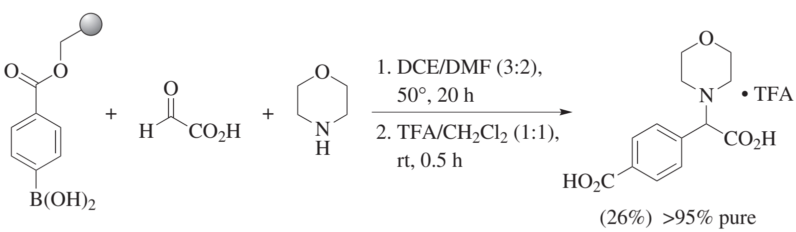
Scheme 18

HFIP as solvent is the most effective, resulting in 85% yield (Eq. 5).[21]

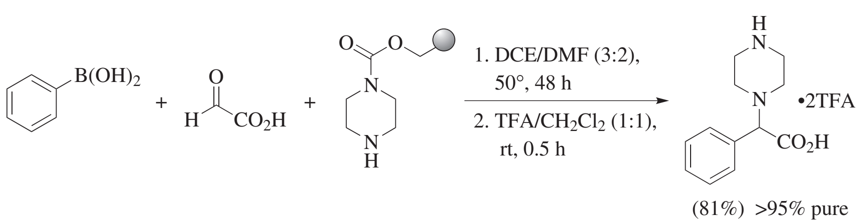


(Eq. 5)

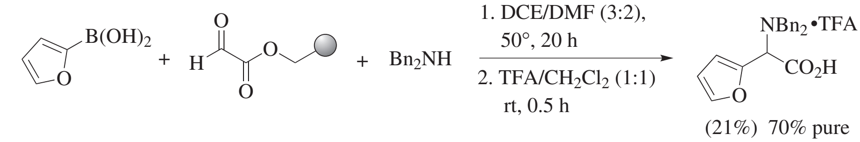
Solid-Phase-Supported Reactions. Solid-phase-supported boronic acid Mannich reactions wherein either the boronic acid component (Eq. 6), the amine component (Eq. 7), or the glyoxylic acid (Eqs. 8 and 9) is anchored to a Wang polystyrene resin have been developed (Tables 1 and 2D).[13] The final α-amino acid or α-amino amide products are released from the resin by cleavage with trifluoroacetic acid (TFA). The product purities are generally high and the yields are good to modest for reactions of a secondary amine or arylboronic acid on the solid support. The yields for the reactions of polymer-supported 2-oxoacetic acid ester (Eq. 8) and amide (Eq. 9) derivatives with 2-furylboronic acid and secondary amines range from 15−37% and product purities range from 59 to 90% (Table 2D).[13]



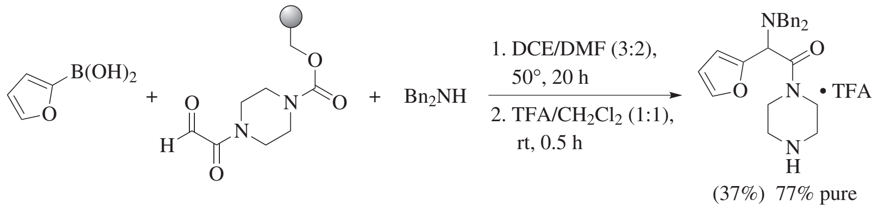
(Eq. 6)



(Eq. 7)

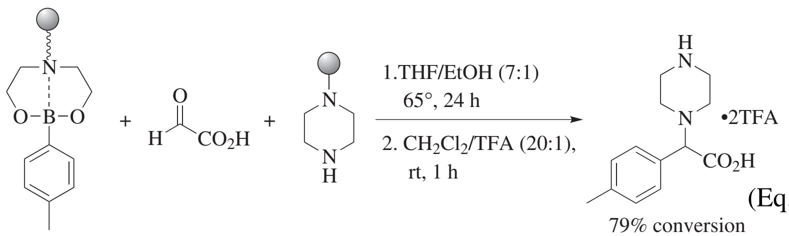


(Eq. 8)



(Eq. 9)

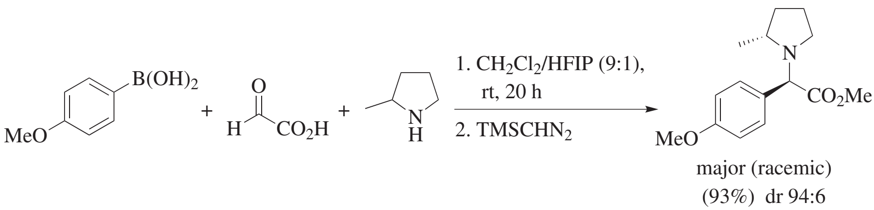
In one study both the organoboron reagent and the amine component are attached to a solid support (Eq. 10).[32]



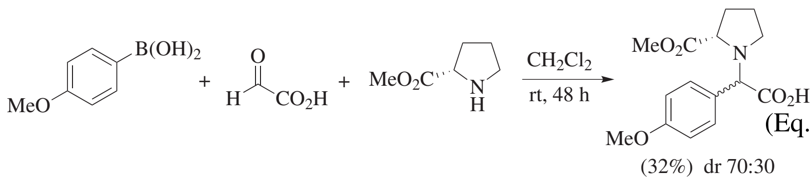
(Eq. 10)

Diastereoselective and Enantioselective Reactions. The diastereoselective synthesis of α-amino acid derivatives having two stereogenic centers has been achieved using enantiomerically pure or racemic amines. The reaction of racemic 2-methylpyrrolidine, glyoxylic acid, and 4-methoxyphenylboronic acid proceeds with high diastereoselectivity (Eq. 11).[18] The reaction of racemic 2-phenylpyrrolidine with glyoxylic acid and phenylboronic acid also proceeds with high diastereoselectivity.[18] A similar reaction using methyl prolinate is less diastereoselective (Eq. 12).[25] (*S*)-2-Phenylglycinol affords the corresponding α-(*E*)-β-styrenyl amino acid derivative with very high diastereoselectivity (Eq. 13).[33] The analogous reaction employing *N*-benzyl-(*R*)-2-phenylglycinol is reported to proceed with high diastereoselectivity (dr 20:1) and affords the corresponding 2-morpholinone arising from a cyclization of the hydroxy acid moieties (Eq. 14).[34] However, the addition of a *para*-substituent on (*E*)-β-styrenylboronic acid renders the reaction significantly less diastereoselective (Table 7E).[34,35] A latter report by the same authors indicates that the high diastereoselectivity of the aforementioned reaction could not be reproduced with a different batch of the boronic acid starting material.[35] In a related study, the reaction of glyoxylic acid, *N*-propargyl-(*S*)-2-phenylglycinol and (*E*)-β-styrenylboronic acid in CH_2Cl_2 gives a 1.5:1 mixture of 2-morpholinone diastereomers (Eq. 15). The

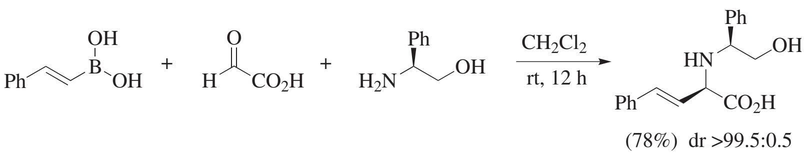
ratio can be increased to 10:0 in favor of the *cis*-product with the addition of Et_3N to the reaction mixture (Table 7E).[36]



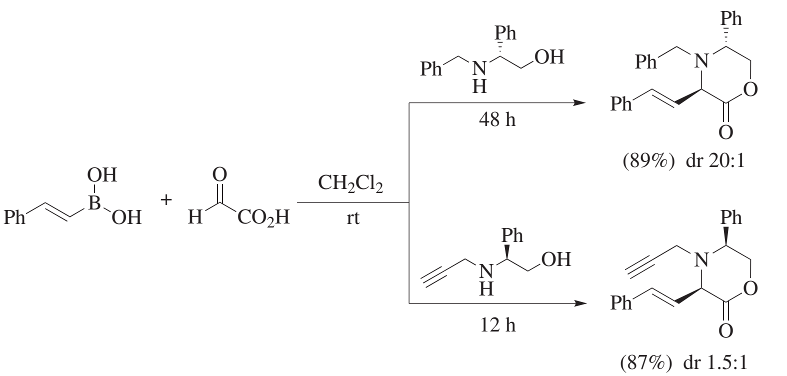
(Eq. 11)



(Eq. 12)



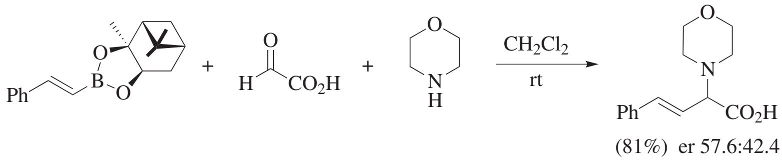
(Eq. 13)



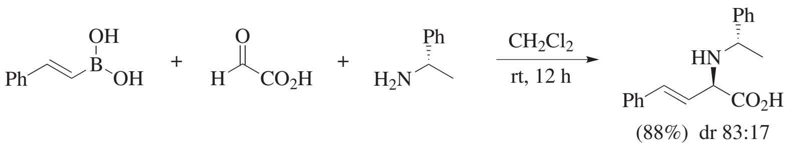
(Eq. 14)

(Eq. 15)

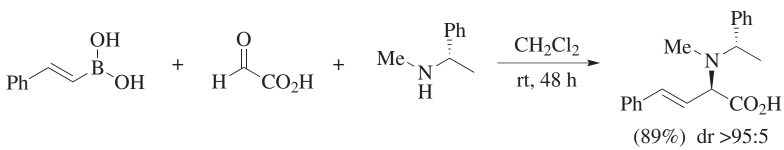
The reactions of various chiral (E)-β-styrenylboronate esters with glyoxylic acid and morpholine provide the corresponding α-amino acids with poor enantioselectivity (er values from 53.0:47.0 to 57.5:42.5) (Eq. 16).[37] The reaction of chiral amine (S)-α-methylbenzylamine with either achiral (E)-β-styrenylboronic acid (Eq. 17),[33] -boronate esters, or chiral (E)-β-styrenylboronate esters give diastereomeric products with poor[31] to modest[31,33] diastereoselectivities. However, the use of secondary amine (S)-α-methyl-N-methylbenzylamine renders all reactions highly diastereoselective, with the reaction using achiral (E)-β-styrenylboronic acid affording the highest chemical yield (89%) (Eq. 18).[31]



(Eq. 16)



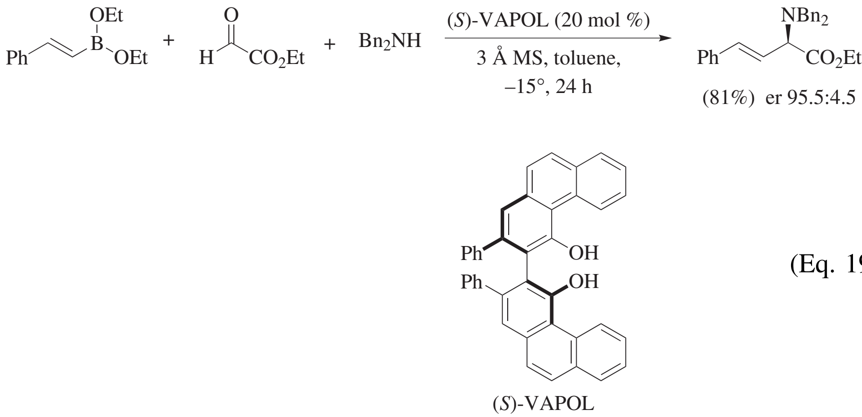
(Eq. 17)



(Eq. 18)

As mentioned earlier, (Z)-2-butenylboronate reacts with glyoxylic acid and ammonia to give a 2,3-*syn*-α-amino acid derivative with almost complete diastereoselectivity (Eq. 4).[28] In situ generated (E)-allylboronates also undergo reactions with glyoxylic acid and aniline, 4-methoxyaniline, or benzhydrylamine to give the corresponding *anti*-α-allylic amino acids with high diastereoselectivities (Scheme 18).[30]

An enantioselective version of the boronic acid Mannich reaction uses ethyl glyoxylate, diethyl 1-alkenylboronate esters, secondary amines, and chiral biphenols as asymmetric catalysts.[38] In the absence of the chiral catalyst, the reaction of ethyl glyoxylate, (E)-β-styrenylboronic acid, and dibenzylamine at $-15°$ in toluene solution (the racemic version of what is shown in Eq. 19) gives the corresponding α-dibenzylamino ester product in 80% yield. Under analogous conditions, except for the use of diisopropyl stryrenylboronate, the yield of the desired product was <5%. Repeating this reaction with the addition of 20 mol % of (S)-BINOL (Chart 1, structure **1a**) results in an enhanced chemical yield (45%) and a product having an er of 60:40. The screening of other catalysts and other (E)-β-styrenylboronate esters identified the biphenol (S)-VAPOL as the best catalyst and diethyl styrenylboronate as the best boronate ester. This combination (Eq. 19) affords a chemical yield of 81% and an er >95:5 for the α-dibenzylamino ester product.[38] This reaction can be extended to include diethyl β-styrenylboronates with substitutions on the phenyl ring, diethyl 1-alkenylboronates ($RCH{=}CHB(OEt)_2$, R = alkyl), and other secondary amines.[38] Chemical yields range from 71–94% and er's from 89:11 to 98.5:1.5 (Table 2B).

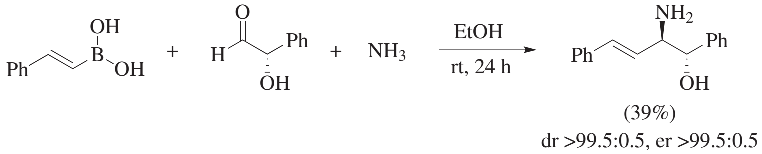


(Eq. 19)

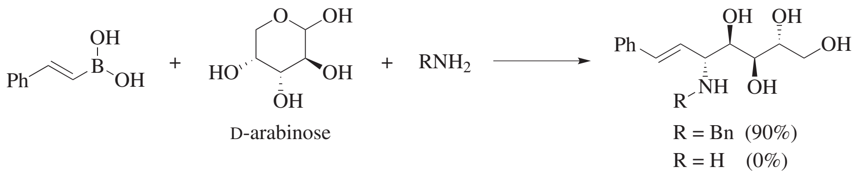
Preparation of *anti*-1,2-Amino Alcohols

The boronic acid Mannich reactions of α-hydroxy aldehydes (or specialized ketones), amines, and aryl- or 1-alkenylboronic acids provide an efficient synthesis of *anti*-1,2-amino alcohols. When chiral α-hydroxy aldehydes are employed these reactions are highly diastereoselective and give *anti*-1,2-amino alcohol products (Eq. 3). Enantioenriched *anti*-1,2-amino alcohol products are obtained when starting with enantioenriched α-hydroxy aldehydes (Table 3).

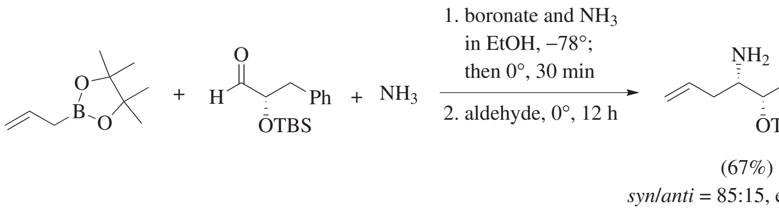
The Amine Component. Ammonia, primary (allylamine, benzylamines, benzhydrylamines, α-substituted and α,α-disubstituted amino acid esters), and secondary amines have been used in these preparations of *anti*-1,2-amino alcohols (Table 3). A single example of the boronic acid Mannich reaction using ammonia as the amine component for the preparation of *anti*-1,2-amino alcohols has been reported. The reaction of (*S*)-2-hydroxyphenylacetaldehyde, ammonia, and (*E*)-β-styrenylboronic acid in ethanol at room temperature for 24 hours gives the corresponding *anti*-1,2-amino alcohol in 39% yield as a single diastereomer (dr >95.5:0.5, er >99.5:0.5) (Eq. 20).[39] Whereas the reaction of D-arabinose with benzylamine and (*E*)-β-styrenylboronic acid gives the desired *anti*-1,2-amino alcohol in 90% yield (the reaction conditions were not described), a similar reaction using ammonia as the amine component is unproductive (Scheme 19).[40] However, the reaction of (*S*)-2-(*tert*-butyldimethylsilyloxy)-3-phenylpropanal, ammonia, and the pinacol ester of allylboronic acid gives the corresponding *O*-protected 1,2-amino alcohol as an 85:15 mixture of *syn* and *anti* isomers in 67% yield (Eq. 21, Table 9).[28] The er of the major *syn* isomer is 97.5:2.5. In this reaction a mechanism similar to that shown in Scheme 5 is clearly not possible and an alternative mechanism involving addition at the γ-carbon of the allylboronate is most likely.



(Eq. 20)



Scheme 19



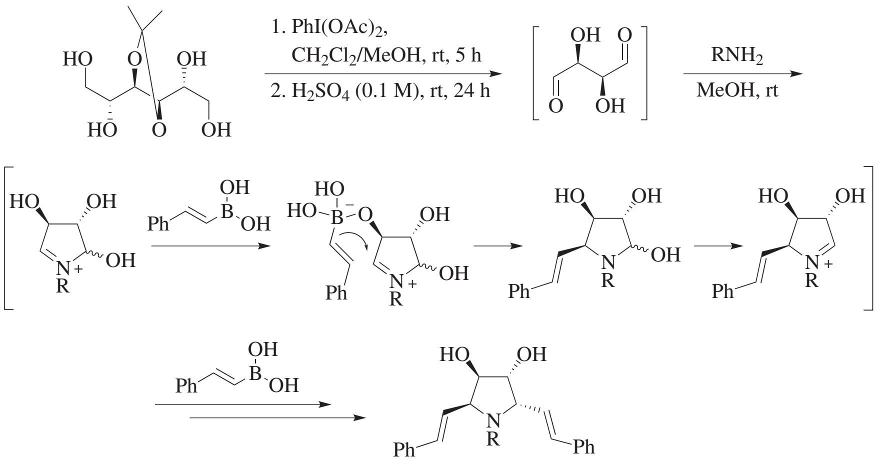
(Eq. 21)

2,3-Dihydroxy-1,4-butanedials and 2,3,4-trihydroxy-1,5-pentanedials, which can be generated by the oxidative cleavage of protected sugars, undergo reactions with ammonia and two equivalents of (*E*)-β-styrenylboronic acid to produce 2,5-di-(*E*)-styrenyl-3,4-dihydroxypyrrolidines and 2,6-di-(*E*)-styrenyl-3,4,5-trihydroxypiperidines, respectively. For example, oxidative cleavage of 3,4-*O*-isopropylidene-D-mannitol with $PhI(OAc)_2$ followed by hydrolysis with 0.1 M H_2SO_4 affords the corresponding 2,3-dihydroxy-1,4-butanedial which upon treatment with (*E*)-β-styrenylboronic acid (2 equiv) and benzylamine or ammonia in MeOH gives the corresponding 2,5-di-(*E*)-styrenyl-3,4-dihydroxypyrrolidines in yields of 65% and 70%, respectively (Scheme 20).[40] In a similar fashion, 1,2-*O*-isopropylidene-D-glucose can be converted to the corresponding 2,6-di-(*E*)-styrenyl-3,4,5-trihydroxypiperidine (Scheme 21).[40] These heterocyclic products could be converted to the corresponding iminocyclitols by ozonolysis of the styrenyl moieties followed by sodium borohydride reduction.

The Organoboron Reagent Component. 1-Alkenyl-, aryl-, and heteroaryl-boronic acids have been used in the preparation of *anti*-1,2-amino alcohols and only a few examples of the use of boronate esters or trifluroboronates are known (Table 3).

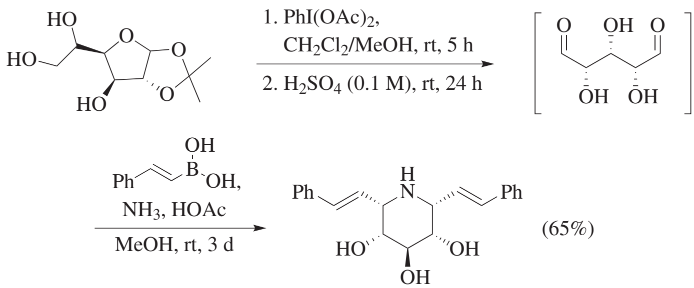
Attempts to perform the boronic acid Mannich reaction between L-arabinose, bis(4-methoxyphenyl)methanamine and vinylboronic acid are thwarted because of the inherent instability of the boronic acid component under the reaction conditions.[41] However, dibutyl vinylboronate works efficiently in ethanol/water

at 50° to provide the desired *anti*-1,2-amino alcohol product, which is isolated as its *N*-acetamide derivative as a single diastereomer, in 55% overall yield (Scheme 22).[41] Water is required in the first reaction to generate an equilibrium concentration of vinylboronic acid in situ.

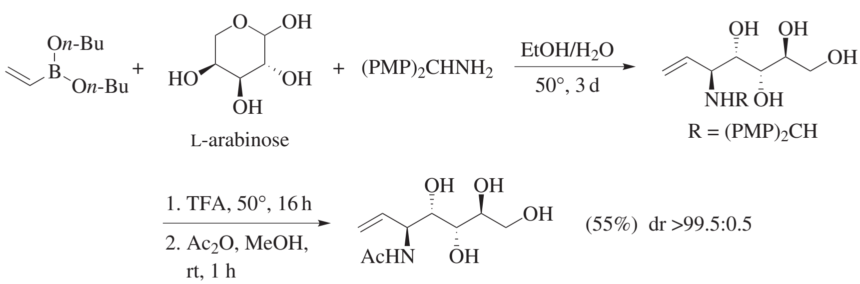


R = Bn (65%)
R = H (70%)

Scheme 20

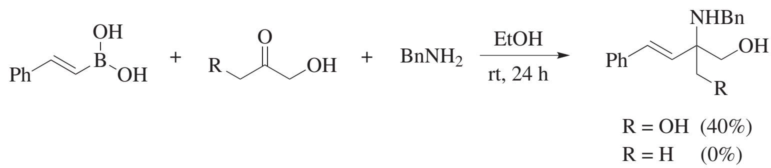


Scheme 21



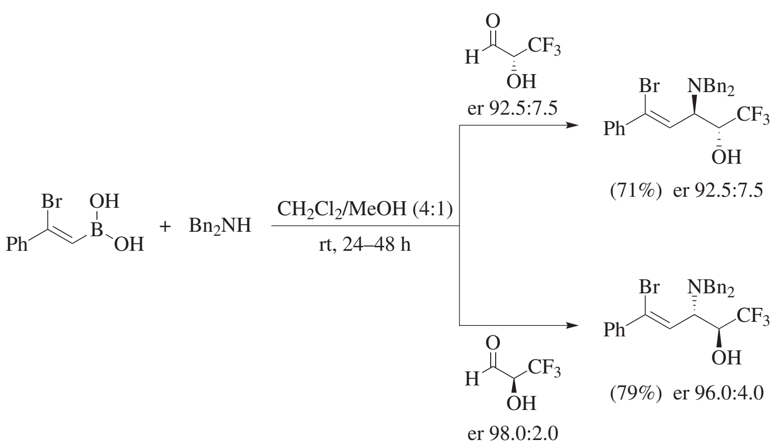
Scheme 22

The Carbonyl Component. Whereas α-hydroxy aldehydes have been successfully employed in the vast majority of cases, α-hydroxy ketones have been less thoroughly investigated. Hydroxyacetone fails to provide an amino alcohol product in its reaction with benzylamine and (*E*)-β-styrenylboronic acid. However 1,3-dihydroxyacetone gives the desired product in 40% yield (Scheme 23).[42]



Scheme 23

Diastereoselective and Enantioselective Reactions. In general, the boronic acid Mannich reactions of α-hydroxy aldehydes and amines with aryl- or 1-alkenylboronic acids provide efficient syntheses of *anti*-1,2-amino alcohols. The reactions of (*R*)- or (*S*)-2-hydroxy-3,3,3-trifluoropropanal with secondary amines or $PMBNH_2$ with aryl- or 1-alkenylboronic acids provide efficient syntheses of *anti*-1,2-amino alcohols with high enantiomeric purities. As a typical example, the reaction of (*R*)-2-hydroxy-3,3,3-trifluoropropanal (er 92.5:7.5) with α-bromo-β-styrenylboronic acid and dibenzylamine affords the corresponding *anti*-1,2-amino alcohol in 71% yield with an er of 92.5:7.5 (Eq. 22).[43] The analogous reaction with (*S*)-2-hydroxy-3,3,3-trifluoropropanal (er 98.0:2.0) gives the *anti*-1,2-amino alcohol product in 79% yield (er 96.0:4.0) (Eq. 23).[43]

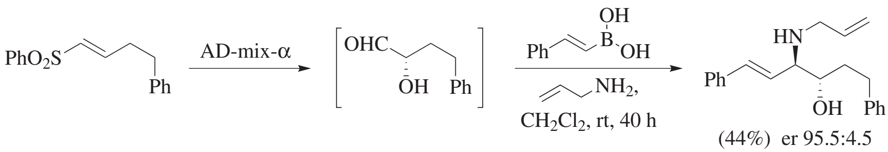


(Eq. 22)

(Eq. 23)

A general method[15,44] of preparing enantioenriched *anti*-1,2-amino alcohols employing enantioenriched α-hydroxy aldehydes formed in situ from the asymmetric dihydroxylation reactions of vinyl sulfones[45] has been developed. For

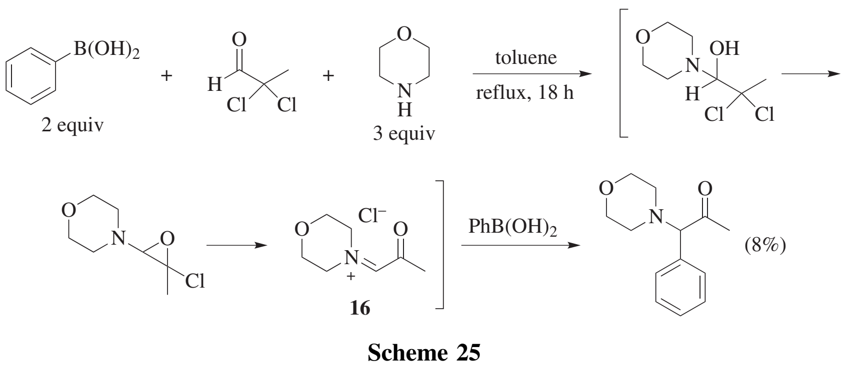
example, the reaction of phenyl (*E*)-4-phenyl-1-butenylsulfone with AD-mix-α followed by treatment of the crude α-hydroxy aldehyde intermediate with allylamine and (*E*)-β-styrenylboronic acid gives the *anti*-1,2-amino alcohol product in 44% overall yield with an er of 95.5:4.5 (Scheme 24).[15]



Scheme 24

Preparation of α-Amino Ketones

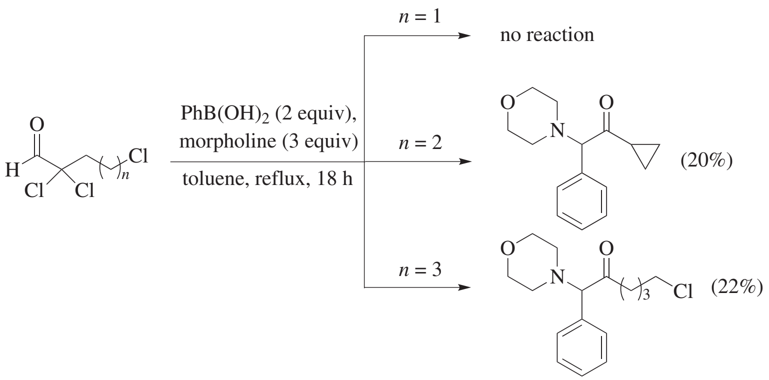
The reactions of α,α-dichloro aldehydes with boronic acids and amines have been studied in a single report (Table 4).[46] The reaction of α,α-dichloropropanal with three equivalents of morpholine and two equivalents of phenylboronic acid gives, under optimized reaction conditions (toluene at reflux for 18 hours), not the boronic acid Mannich product but 1-morpholinyl-1-phenylpropanone (Scheme 25).[46] The yield as determined by GC−MS is 50% while the isolated yield is only 8%. The proposed mechanism involves iminium ion **16** (Scheme 25). The yields are slightly improved (12−23%) when more electron-rich phenylboronic acids are employed, whereas 4-chlorophenylboronic acid and 3-nitrophenylboronic acid give the corresponding α-amino ketones in 2% yield and trace amounts, respectively.



Scheme 25

Other short-chain α,α-dichloro aldehydes ($RC(Cl)_2CHO$, R = Et, *i*-Pr, and *n*-C_5H_{11}) react under similar conditions with phenylboronic acid to provide analogous α-amino ketones in poor yields, ranging from 10−24%, and the reactions of longer-chain α,α-dichloroaldehydes (R = *n*-$C_{10}H_{21}$ and *n*-$C_{16}H_{33}$) are even less efficient (yields 0.3−1%).[46] Other secondary amines (both cyclic and acyclic) are not effective and the use of benzylamine only results in formation of the unreactive imine. The reactions of α,α,ω-trichloro aldehydes (n = 1−3) were also studied (Eqs. 24−26).[46] No reaction takes place when n = 1, whereas the

expected α-amino ketone is obtained in 22% yield when $n = 3$ (Eq. 26). When $n = 2$ the expected product undergoes a base-catalyzed cyclization to a cyclopropyl ketone (Eq. 25).

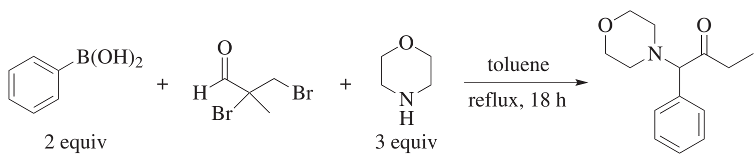


(Eq. 24)

(Eq. 25)

(Eq. 26)

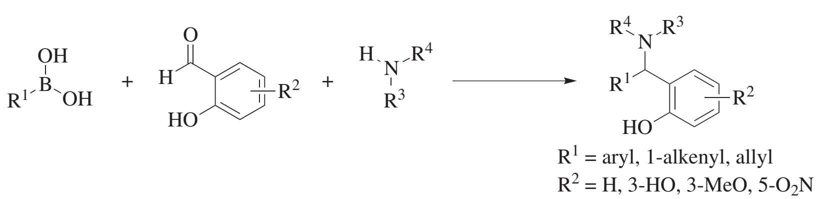
2,3-Dibromo-2-methylpropanal gives the same α-amino ketone product (Eq. 27) as is obtained from the reaction of α,α-dichlorobutanal with phenylboronic acid and morpholine.[46] A mechanism has been proposed that involves a 1,2-methyl shift.[46]



(Eq. 27)

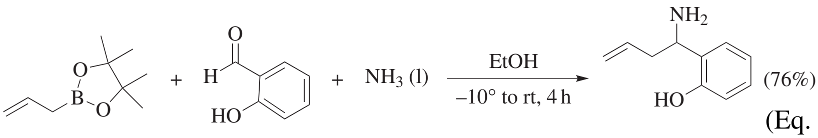
Preparation of 2-Hydroxybenzylamines and Derivatives

The boronic acid Mannich reactions of substituted 2-hydroxy aromatic aldehydes (substituted salicylaldehydes), amines, and aryl-, 1-alkenyl-, or allylboronic acids provide efficient syntheses of 2-hydroxybenzylamine derivatives (Scheme 26). The substituent R^2 on the aromatic ring can be H, 3-OH, 3-OMe, or 5-NO_2 (Table 5). When the corresponding 2-methoxy aromatic aldehydes are employed these reactions are unsuccessful.[47,48] The reaction of 2-hydroxyacetophenone, morpholine, and phenylboronic acid is also unproductive.[47] Reactions involving 1-alkenylboronic acids are normally performed at room temperature in ethanol;[14] higher temperatures result in the formation of 2*H*-chromene derivatives.[47]



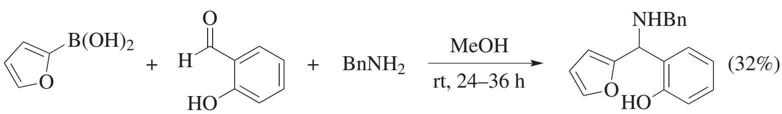
Scheme 26

The Amine Component. Liquid ammonia has been employed in a single example as the amine component in the reaction of salicylaldehyde with an allylboronate (Eq. 28).[28] Aqueous ammonia (25%) can also be used when 4-dodecylbenzenesulfonic acid (DBSA) is added to the reaction mixture.[49]



(Eq. 28)

Primary amines (allylamine, benzylamine, 4-methylaniline, and benzhydrylamine) have been used with limited success.[14] The use of the pinacol ester of (E)-β-styrenylboronic acid in the reaction of benzylamine and salicylaldehyde is unproductive.[21] Use of the more reactive 2-furanylboronic acid affords the desired product in only 32% yield (Eq. 29).[14] The reactions of salicylaldehyde and phenylboronic acid with 4-methylaniline or benzhydrylamine result in formation of only the corresponding imines.[50]

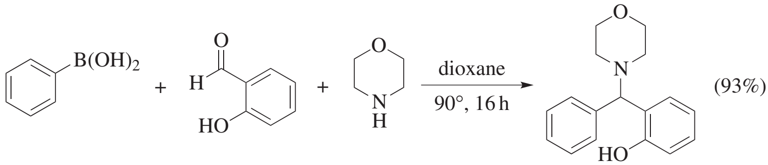


(Eq. 29)

In contrast, the reactions of substituted 2-hydroxy aromatic aldehydes and secondary aliphatic cyclic and acylic amines with aryl- and 1-alkenylboronic acids generally provide efficient syntheses of 2-hydroxybenzylamines (Table 5).

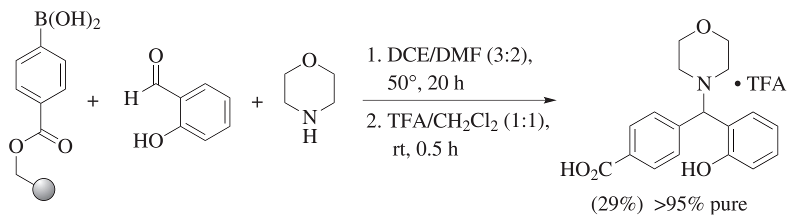
The Organoboron Reagent Component. A variety of aryl-, heteroaryl-, and 1-alkenylboronic acids have been used successfully in the preparation of 2-hydroxybenzylamines. The use of boronate esters (Eq. 28) or potassium organotrifluoroborates[48] has been very limited.

Solvent Effects. Studies of the effects of the solvent on the reaction between salicylaldehyde, morpholine, and phenylboronic acid have been reported from four different laboratories.[16,47,50,51] Under microwave heating, solvent-free conditions[51] work equally well as the use of dichloromethane as the solvent.[50] Conventional heating under solvent-free conditions[51] or using dipolar aprotic (DMF),[16] protic (water, ethanol),[16] relatively nonpolar aprotic (dioxane,[47] DME,[16] and DCE[16]), and nonpolar (toluene) solvents[16] gives the Mannich product in yields ranging from 41–93%. The best yield is obtained using dioxane at 90° for 16 hours (Eq. 30)[47] whereas the lowest yield is obtained when DMF is employed at 80° for 5 hours.[16] An ionic liquid is reported to enhance the rate and yield of the reaction compared to the same reaction using methanol at room temperature.[52]

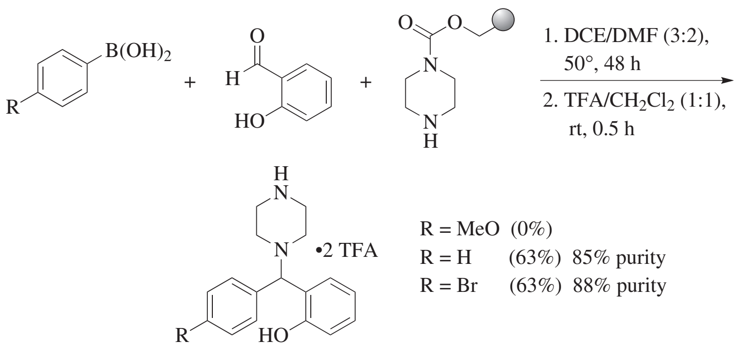


(Eq. 30)

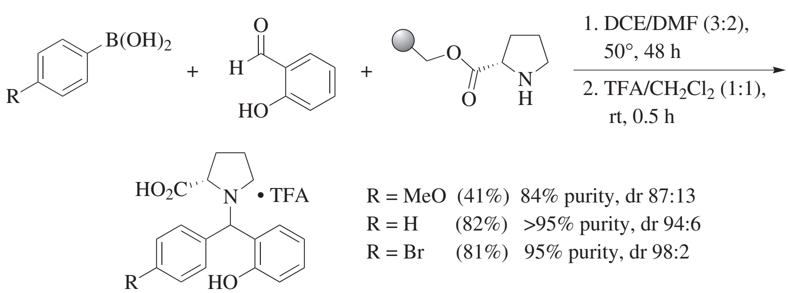
Solid-Phase-Supported Reactions. Syntheses of 2-hydroxybenzylamines that employ either the boronic acid component (Eq. 31)[13] or the amine component (Schemes 27[13] and 28[13]) anchored to a solid support have been developed (Table 5). The final 2-hydroxybenzylamine products are released from the resin by cleavage with TFA. The product purities are generally high and the yields are poor to modest. A solid-supported chiral proline allows for the diastereoselective synthesis of *N*-unsymmetrical diarylmethylproline derivatives (Scheme 28).[13]



(Eq. 31)



Scheme 27

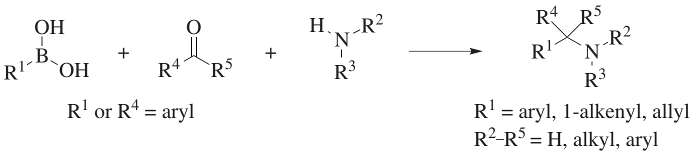


Scheme 28

Diastereoselective Reactions. For the diastereoselective synthesis of *N*-unsymmetrical diarylmethylproline derivatives see Scheme 28 above.[13]

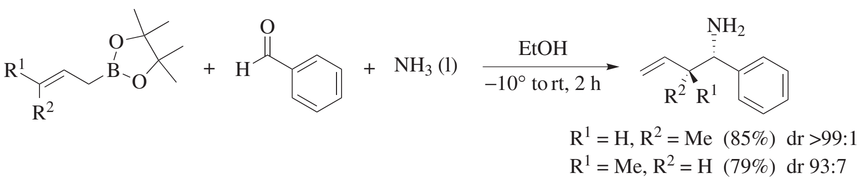
Preparation of Aminomethylarenes

The boronic acid Mannich reactions of aldehydes or ketones, amines, and aryl-, 1-alkenyl- or allylboronic acids provide efficient syntheses of aminomethylarenes (Scheme 29) when either the carbonyl or the boronic acid component is aromatic (Table 6).



Scheme 29

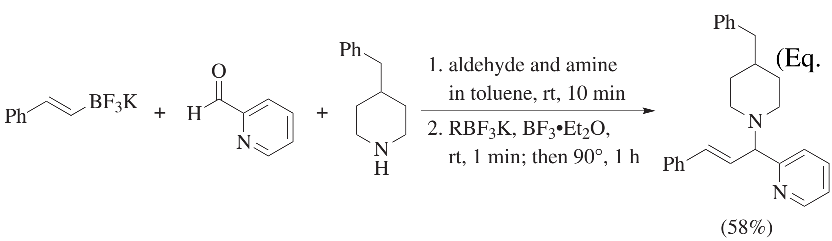
The Amine Component. Liquid ammonia or aqueous ammonia (25%), often in the presence of DBSA,[49] has been successfully employed as the amine component in the reaction of aromatic aldehydes or ketones with allylic boronates (R^1 = H, Me; R^2 = H, Me).[28] Addition at the γ-carbon of the allylic boronates affords the product α-allylic aminomethylarenes in yields ranging from 75–96% when liquid ammonia is used (Scheme 30).[28]



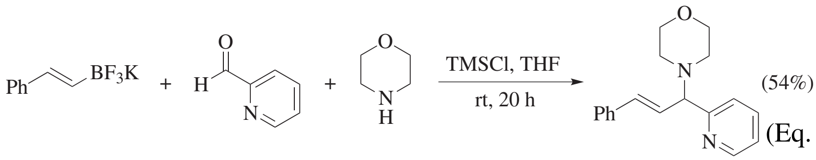
Scheme 30

Other primary amines have not been examined with allylic boronates or arylboronic acids or esters. The majority of successful examples employ secondary aliphatic cyclic and acyclic amines (Table 6).

The Organoboron Reagent Component. A variety of aryl-, heteroaryl-, and 1-alkenylboronic acids or the corresponding potassium trifluoroborates have been used successfully in the preparation of aminomethylarenes. The use of boronate esters[28,49] has been limited to allylic boronates (Scheme 30). In the case of potassium (*E*)-β-styrenyltrifluoroborate a Lewis acid (BF_3•Et_2O[48] or TMSCl[53]) is necessary to achieve acceptable yields (Eqs. 32 and 33).



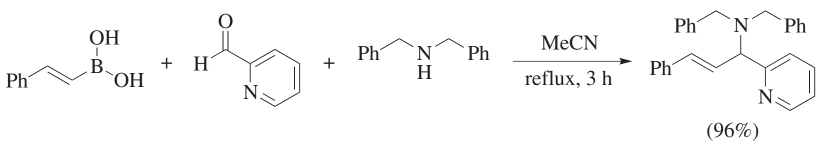
(Eq. 32)



(Eq. 33)

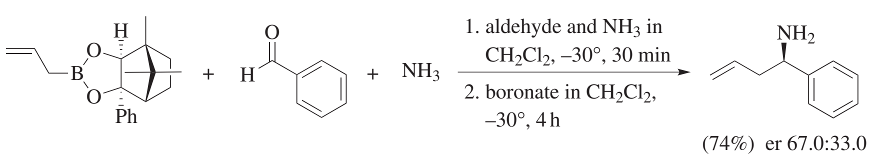
The Carbonyl Reagent Component. In general, the reactions of paraformaldehyde, secondary amines, and arylboronic acids or potassium aryltrifluroborates work efficiently; the latter organoboron reagents usually requiring the use of a Lewis acid (BF_3•Et_2O[48] or TMSCl[53]). Aliphatic aldehydes work well with the highly reactive 2-furanylboronic acid (Scheme 1)[2] but other studies using aliphatic aldehydes have not been published. Aryl and heteroaryl aldehydes lacking an *ortho*-hydroxy group are generally unreactive except towards allylic boronic acids and boronates. 2-Pyridinecarboxaldehyde and its derivatives are exceptions (Eqs. 32 and 33).[48,53] Allylic boronates also efficiently participate in reactions with aryl methyl ketones or 9*H*-fluoren-9-one and ammonia.[29]

Solvent Effects. A study of the effects of the solvent on the reaction between 2-pyridinecarboxaldehyde, dibenzylamine, and (*E*)-β-styrenylboronic acid has been reported.[54] At room temperature, acetonitrile is the best solvent at 0.1 M. The best conditions are 0.2 M in acetonitrile at reflux temperature, resulting in a yield of 96% (Eq. 34).



(Eq. 34)

Diastereoselective and Enantioselective Reactions. The diastereoselective syntheses of *syn* (dr >99:1) and *anti* (dr 93:7) homoallylic amines from the reactions of (*Z*)- and (*E*)-2-butenyl-1-boronates, respectively, are described above (Scheme 30).[28] The synthesis of a homoallylic amine using a chiral allylboronate proceeds with poor enantioselectivity (er 67.0:33.0) (Eq. 35).[28]

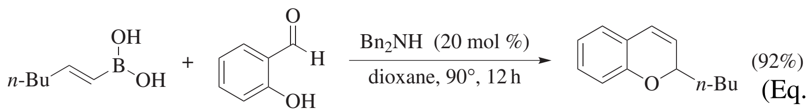


(Eq. 35)

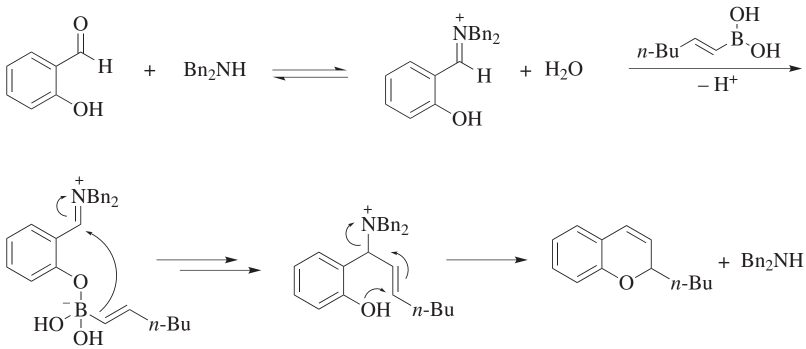
Preparation of Heterocycles

Synthesis of 2*H*-Chromenes. The reactions of substituted 2-hydroxy aromatic aldehydes (substituted salicylaldehydes), amines, and 1-alkenylboronic

acids provide efficient syntheses of $2H$-chromene derivatives (Eq. 36 and Table 7A).[47,55–59] These reactions can be substoichiometric in the amine component which is consistent with the mechanism proposed in Scheme 31.[47,56]

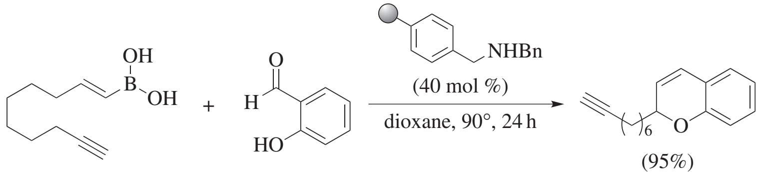


(Eq. 36)



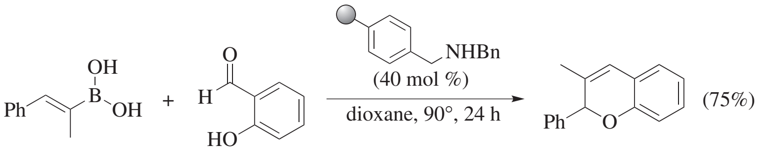
Scheme 31

The Amine Component. Dibenzylamine (20 mol%) is the most commonly employed amine for the synthesis of $2H$-chromenes; however, diethylamine has also been found effective.[16,47,55,56] A polystyrene-supported dibenzylamine (40 mol %) is also effective (Eq. 37).[47] Some tertiary amines have also been employed (e.g., Et_3N, i-Pr_2NEt, and DABCO); however, reaction rates are much slower and yields are lower.[55] In examples using a tertiary amine, a different mechanism to that in Scheme 31 must be operating, perhaps involving addition of the 1-alkenyl group to the carbonyl group of salicylaldehyde followed by cyclization via the aromatic hydroxy group with concomitant loss of water.

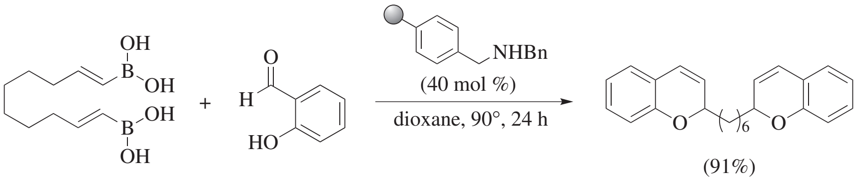


(Eq. 37)

The Organoboron Reagent Component. A variety of ($1E$)-alkenylboronic acids or their corresponding potassium trifluoroborates[55,57] have been successfully used to prepare $2H$-chromenes (Eq. 36 and 37, Table 7A), including an α-substituted alkenylboronic acid (Eq. 38).[47] In one case a bis-boronic acid provides the corresponding bis-$2H$-1-benzopyran (Eq. 39).[47] The use of 1-alkenylboronate esters has not been reported.

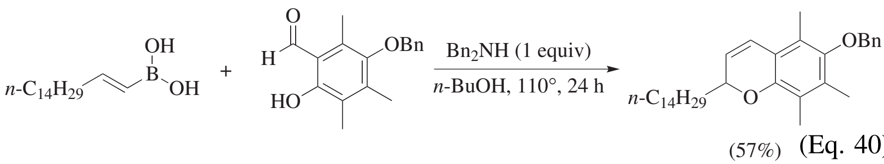


(Eq. 38)



(Eq. 39)

The Carbonyl Reagent Component. Substituted salicylaldehydes have been successfully employed, including those with electron-donor and acceptor groups and relatively hindered ones (Eq. 40).[55]

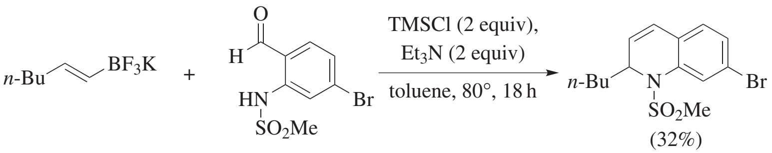


(Eq. 40)

Solvent Effects. Dioxane,[47,56] DMF,[57] and water[16,55,56] are commonly used as well as ionic liquids.[58] The hindered aldehyde shown in Eq. 40 requires relatively forcing conditions: heating in 1-butanol at 110° for 24 hours.[55]

Solid-Phase-Supported Reactions. Solid-phase-supported dibenzylamine catalyses the synthesis of $2H$-chromenes with a catalyst loading of 40 mol % (Eq. 37–39). The yields are generally high (75–99%, Table 7A).[47]

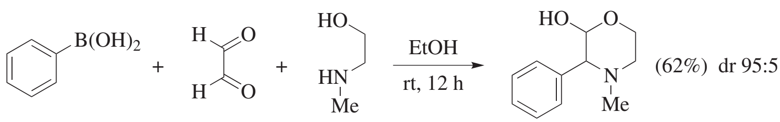
Synthesis of 1,2-Dihydroquinolines. The reactions of 2-sulfamidobenzaldehyde derivatives and potassium 1-alkenyltrifluoroborates in the presence of two equivalents of triethylamine and two equivalents of TMSCl in toluene with heating at 80° provide 1,2-dihydroquinoline derivatives (Eq. 41 and Table 7B).[55] A mechanistic scheme has been proposed in which the penultimate intermediate is related to that shown in Scheme 31.[55] In examples using a tertiary amine, a different mechanism to that in Scheme 31 must be operating. The authors have suggested that the tertiary amine adds to the aldehyde of the 2-sulfamidobenzaldehyde followed by a dehydration step, assisted by the ring sulfamide. The resulting intermediate is then attacked by the vinylic boronic acid, giving an intermediate related to the penultimate intermediate in Scheme 31. They considered this mechanism more likely than one involving addition of the 1-alkenyl group to the aldehyde carbonyl followed by cyclization via the aromatic sulfamido group with concomitant loss of water.



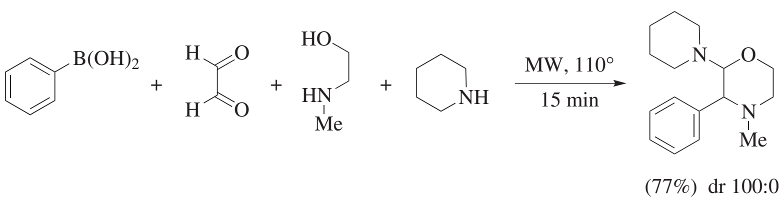
(Eq. 41)

The Carbonyl Reagent Component. Substituted 2-sulfamidobenzaldehydes having electron donor (4,5-dimethoxy) and acceptor groups (4-bromo and 5-nitro) have been successfully employed.[55]

Synthesis of 2-Hydroxy- and 2-Aminomorpholines. The reactions of glyoxal and derivatives with boronic acids and 1,2-amino alcohols give 2-hydroxymorpholines (Eq. 42).[59] However, addition of a secondary amine as the fourth reaction component leads to 2-aminomorpholines (Eq. 43 and Table 7C).[60] In many reactions, including those shown below, the relative configurations of the products were not determined.

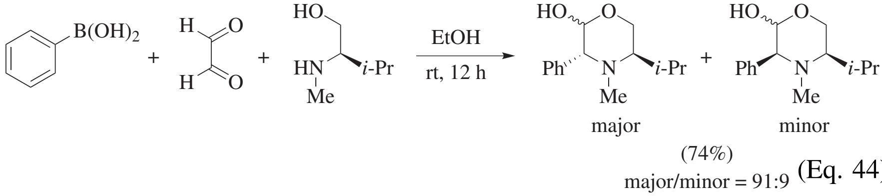


(Eq. 42)



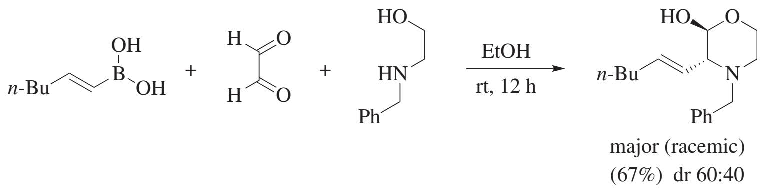
(Eq. 43)

The 1,2-Amino Alcohol Component. *N*-allyl-,[59] *N*-benzyl-,[56,59,61] and *N*-methylethanolamine[59–61] have been used along with their C-1 or C-2 alkyl- (Eq. 44) or phenyl-substituted analogues.[59]



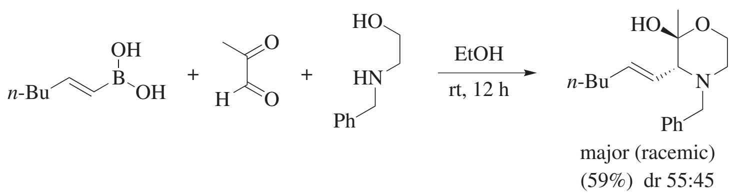
(Eq. 44)

The Organoboron Reagent Component. A variety of 1-alkenyl- (Eq. 45)[59] and arylboronic acids have been successfully used in the synthesis of 2-hydroxy- and 2-aminomorpholines.[56,59–61]



(Eq. 45)

The Carbonyl Reagent Component. Pyruvaldehyde (Eq. 46) and 2-oxo-2-phenylacetaldehyde can be used instead of glyoxal to give 3-methyl- and 3-phenyl-substituted derivatives, respectively.[59,61]

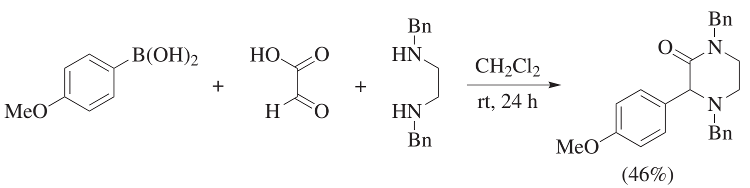


(Eq. 46)

Solvent Effects. Ethanol at room temperature is most commonly used to prepare 2-hydroxymorpholines (Eq. 42)[59] whereas the synthesis of 2-aminomorpholines requires microwave heating at 110° in the absence of solvent for 15 minutes (Eq. 43).[60]

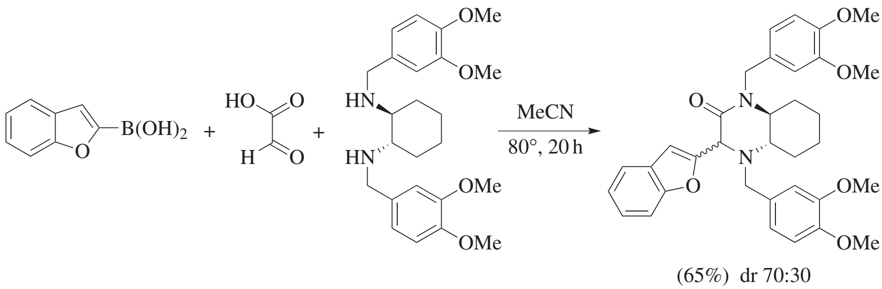
Diastereoselective Reactions. These reactions are often highly diastereoselective, including when a chiral 1,2-amino alcohol is used (Eqs. 42–44).[59] However, some reactions involving *N*-benzyl-1,2-amino alcohols are poorly diastereoselective (Eqs. 45 and 46).

Synthesis of Piperazinones. Reactions of glyoxylic acid with boronic acids and 1,2-diamines give piperazinones (Eq. 47 and Table 7D).[62]



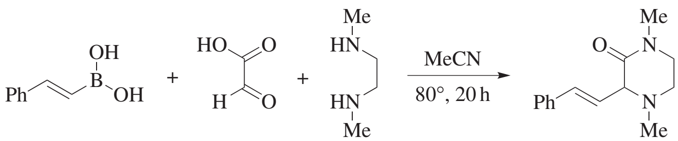
(Eq. 47)

The 1,2-Diamine Component. *N*,*N'*-Dimethylethylenediamine,[62] *N*,*N'*-dibenzylethylenediamine,[38,62] and *N*,*N'*-diisopropylethylenediamine[62] have been successfully employed. (1*S*,2*S*)-*N*,*N'*-bis[(3,4-Dimethoxyphenyl)methyl]-1,2-cyclohexanediamine upon reaction with glyoxylic acid and 2-furylboronic acid gives the corresponding piperazinone product, with undefined configuration at the newly formed stereocenter, as a 70:30 mixture of diastereomers (Eq. 48).[62]



(Eq. 48)

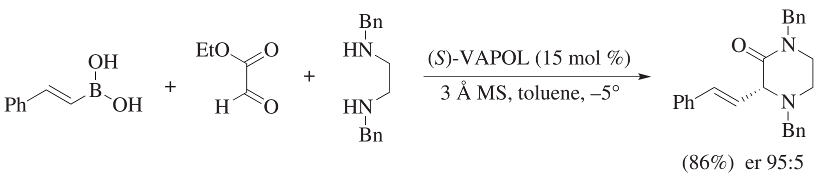
The Organoboron Reagent Component. (*E*)-β-Styrenylboronic acid (Eq. 49) and its corresponding diethyl ester,[38,62] activated phenylboronic acids (3,4-dimethoxy- and 4-methoxyphenylboronic acids (Eq. 47)), and heterocyclic aromatic boronic acids (Eq. 48)[62] have been successfully used for the preparation of piperazinones (Table 7D).



(50%) (Eq. 49)

Solvent Effects. Acetonitrile is used most commonly as the reaction solvent, with heating at 80° required for several hours.[62]

Diastereoselective and Enantioselective Reactions. A diastereoselective reaction has been reported using a chiral diamine, however the diastereoselectivity is modest (dr 70:30) (Eq. 48).[62] The use of the chiral catalyst (*S*)-VAPOL (see Eq. 19 for structure) allows for the synthesis of the corresponding piperazinone with an er of 95:5 (Eq. 50).[38]



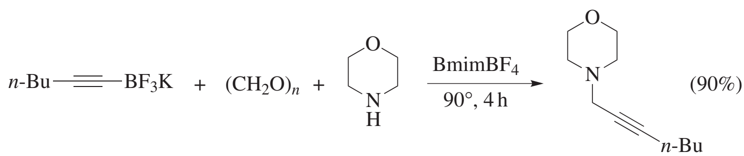
(Eq. 50)

Synthesis of 2-Morpholinones. In a limited study the reactions of glyoxylic acid, *N*-benzyl-(*R*)-2-phenylglycinol and *N*-propargyl-(*S*)-2-phenylglycinol, and (*E*)-β-styrenylboronic acid in CH_2Cl_2 gives mixtures of 2-morpholinone diastereomers (Eqs. 14 and 15). See Table 7E for other examples.[34–36]

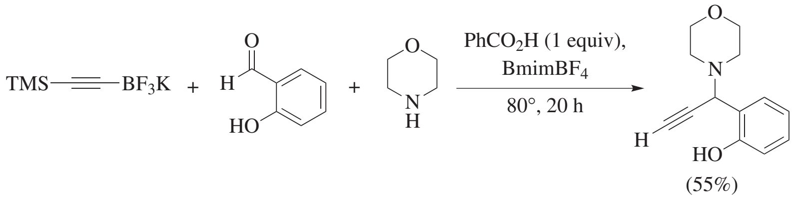
Preparation of Propargylic Amines

The reactions of formaldehyde or substituted salicylaldehydes with 1-alkynyltrifluoroborates and secondary amines afford propargylamines (Eqs. 51 and 52).[63]

These reactions are best performed using the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) at 80–90°. Those reactions involving substituted salicylaldehydes often require the presence of one equivalent of benzoic acid (Table 8).



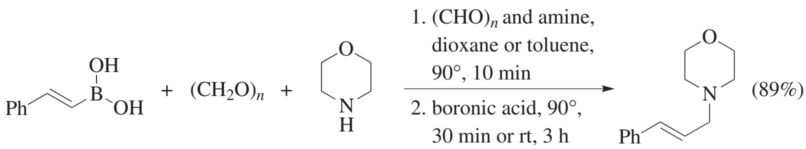
(Eq. 51)



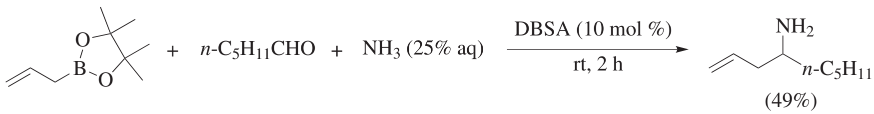
(Eq. 52)

Preparation of Allylic and Homoallylic Amines

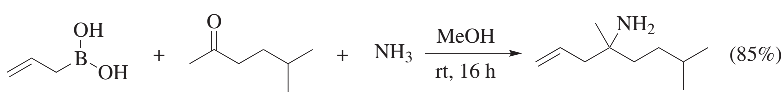
The reactions of formaldehyde with 1-alkenylboronic acids[7,64] or trifluoroborates[48] and secondary amines give allylic amines (Eq. 53).[7] The reactions of aldehydes (Eq. 54)[49] or ketones (Eq. 55)[29] with allylic boronic acids, boronates, or potassium trifluoroborates and ammonia, or in one case a secondary amine,[48] afford homoallylic amines (Table 9).



(Eq. 53)

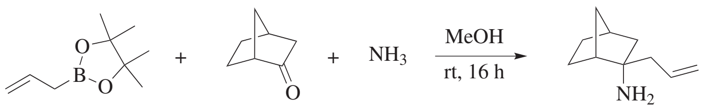


(Eq. 54)



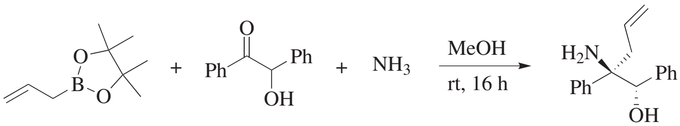
(Eq. 55)

Diastereoselective Reactions. The reaction of bicyclo[2.2.1]heptan-2-one, ammonia, and the pinacol ester of allylboronic acid affords a 94:6 mixture of the *endo*- and *exo*- amine products (Eq. 56).[29] Under the same reaction conditions, 2-hydroxy-1,2-diphenylethanone gives the corresponding 1,2-amino alcohol in 81% yield and 88:12 diastereomeric ratio (Eq. 57).[29]



major (racemic)
(91%) dr 94:6

(Eq. 56)



major (racemic)
(81%) dr 88:12

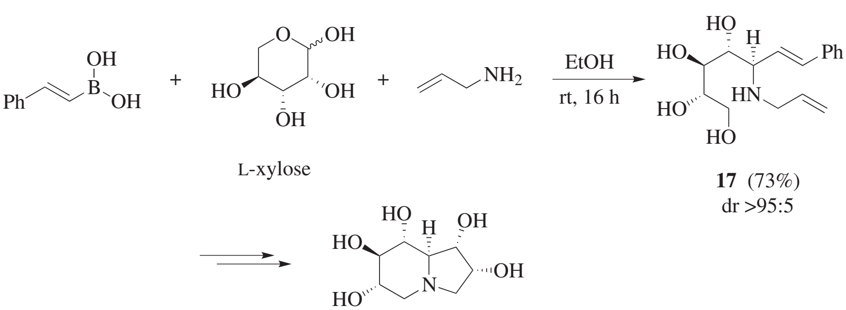
(Eq. 57)

APPLICATIONS TO SYNTHESIS

The 1,2-amino alcohol products derived from the reactions of 1-alkenylboronic acids, α-hydroxy aldehydes, and amines have found applications in amino sugar and alkaloid synthesis. The acetamidotetrol product shown in Scheme 22 could be converted in two synthetic steps to L-*N*-acetylneuraminic acid.[41] Other sialic acids and derivatives could be prepared starting from different sugar starting materials.

The tetrasubstituted pyrrolidine product shown in Scheme 20 and related compounds are readily converted to iminocyclitols after oxidative cleavage of the styrenyl groups followed by reduction with $NaBH_4$.[40]

The boronic acid Mannich reaction of L-xylose, (*E*)-β-styrenylboronic acid, and allylamine gives the amino tetrol **17** which is converted to the proposed structure of the alkaloid uniflorine A (Scheme 32).[65] A comparison of the NMR data of the synthetic and natural compounds indicated that the proposed structure of the natural product is incorrect. Further synthetic studies (Scheme 33) revealed that the natural product is indeed a 2-hydroxymethylpyrrolizidine rather than an indolizidine.[66,67] Compound **17** also serves as a precursor to other 2-hydroxymethylpyrrolizidine alkaloids, including casuarine, australine, and 3-*epi*-australine (Scheme 33)[67] and castanospermine.[68]

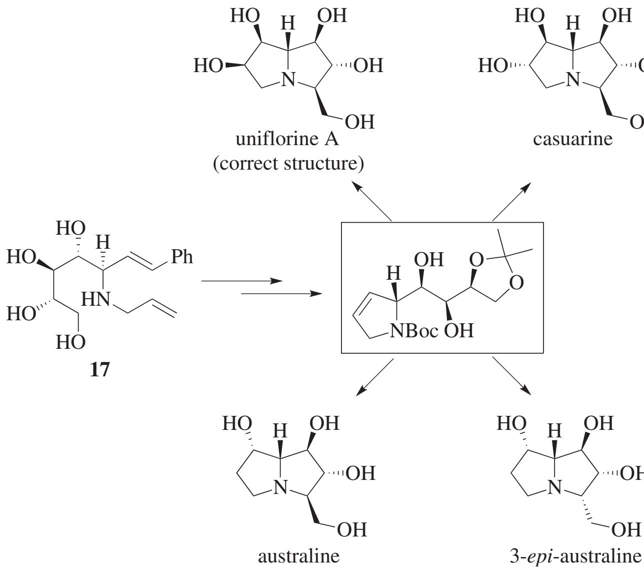


L-xylose

17 (73%)
dr >95:5

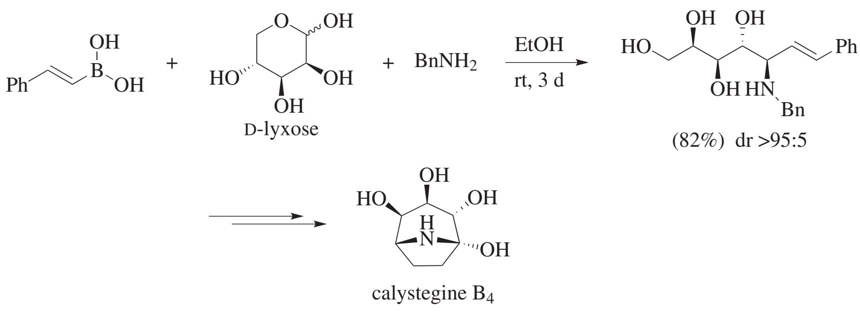
proposed structure of
uniflorine A

Scheme 32



Scheme 33

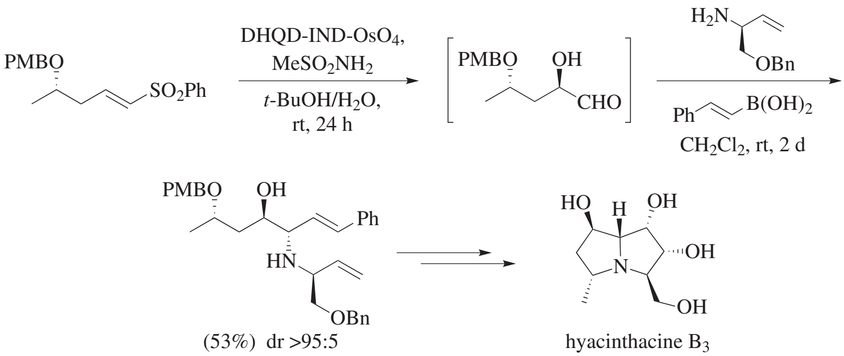
A synthesis of the nortropane alkaloid calystegine B_4 can be achieved in 10 steps from D-lyxose using the boronic acid Mannich reaction in the first step (Scheme 34).[69]



Scheme 34

The pyrrolizidine alkaloid hyacinthacine B_3 has been prepared using the boronic acid Mannich reaction as one of the key steps to provide an 1,2-amino alcohol containing four of the stereogenic carbons of the target molecule (Scheme 35).[44]

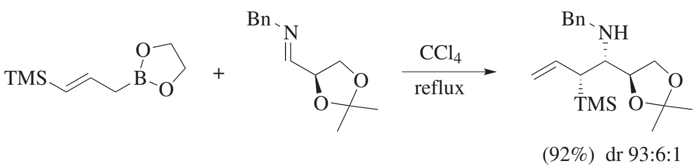
The one-step reaction of salicylaldehydes with amines and 1-alkenylboronic acids or 1-alkenyltrifluoroborates affords 2*H*-chromenes (2*H*-1-benzopyrans). This process has been applied to a concise synthesis of a tocopherol analogue (Eq. 40).[55]



Scheme 35

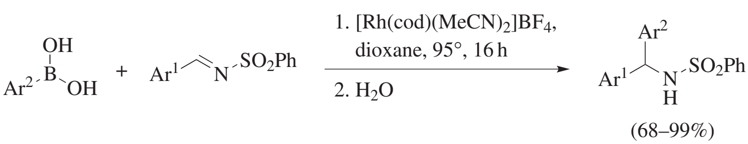
COMPARISON WITH OTHER METHODS

Homoallylic amines can be prepared by the reactions of allylboronates with aryl or alkyl *N*-alkyl aldimines, however these reactions require an excess of the boronate reagent (2–8 equivalents) and heating at reflux in toluene or CCl_4 solution for several days.[70] These reaction proceed via addition to the γ-carbon of the boronate, and can be highly diastereoselective when chiral *N*-benzyl aldimines are employed (Eq. 58).[70]



(Eq. 58)

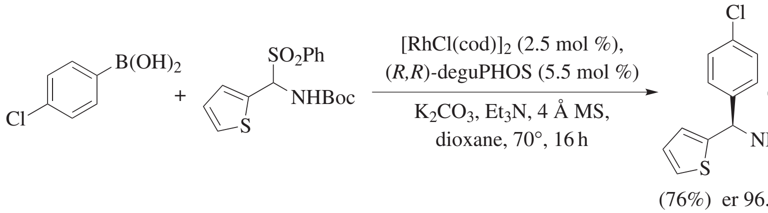
The rhodium-catalyzed addition of arylboronic acids to aromatic *N*-phenylsulfonyl aldimines occur under relatively milder reaction conditions (95°, dioxane, 16 hours) to afford *N*-sulfonyldiarylmethylamines, generally in good yields (68–99%) (Eq. 59).[71] The corresponding reactions of the *N*-benzenesulfonyl aldimines of cyclohexanecarboxaldehyde and cinnamaldehyde also proceed efficiently. *N*-Phenyl aldimines, however, are not reactive.[71]



(Eq. 59)

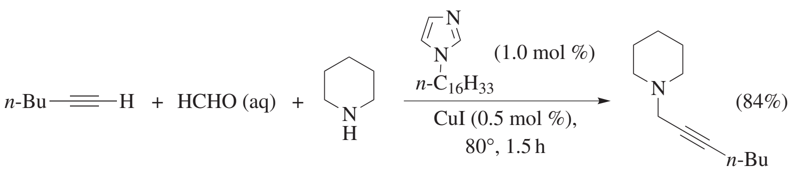
The enantioselective versions of these reactions have been developed using rhodium (or other metals) with chiral ligands.[72–79] Most of these methods are limited to aromatic imines, but more recently enantioselective catalytic additions to

aliphatic imines have also been reported.[80] These methods, however, often require the synthesis of relatively unstable imine starting materials or require harsh conditions to remove the *N*-substituent present in the final addition products. A solution to these problems is the use of *N*-Boc aromatic imines that are generated in situ from easily prepared and stable α-carbamoyl sulfones.[81,82] Commercially available (3*R*,4*R*)-1-benzyl-3,4-bis-diphenylphosphanylpyrrolidine ((*R*,*R*)-deguPHOS) is used as the chiral ligand and $[RhCl(cod)]_2$ as the precatalyst to provide *N*-Boc-protected amine products in enantiomeric ratios up to 99.5:0.5 (Eq. 60).[82]



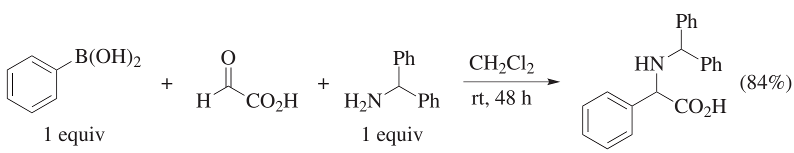
(Eq. 60)

Propargylic amines are readily prepared by the copper-catalyzed reactions of aryl and alkyl terminal alkynes, paraformaldehyde, and secondary amines.[83–85] A recent study shows that the yields of these reactions can be significantly enhanced by the addition of *N*-alkylimidazole ligands (Eq. 61).[85]



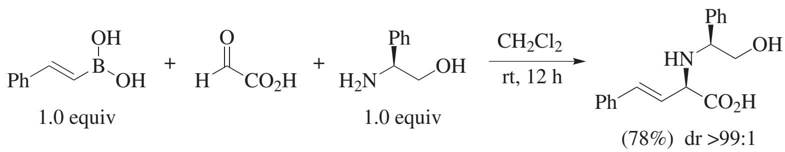
(Eq. 61)

EXPERIMENTAL PROCEDURES

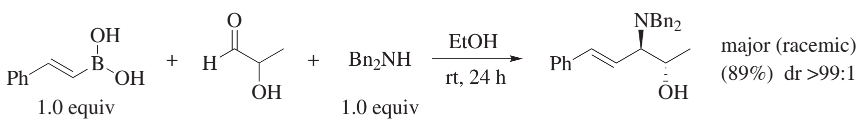


(±)-*N*-(Diphenylmethyl)-α-phenylglycine [Preparation of α-Arylglycine Derivatives from Glyoxylic Acid].[86] To a stirred solution of glyoxylic acid monohydrate (92 mg, 1 mmol) in CH_2Cl_2 (7 mL) was added benzhydrylamine (183 mg, 1.0 mmol), followed by phenylboronic acid (122 mg, 1.0 mmol). After the flask was purged with argon and sealed, the reaction mixture was stirred vigorously at rt for 48 h. The resulting precipitate was isolated by filtration, washed with CH_2Cl_2 (10 mL), and purified by ion-exchange chromatography (Dowex 50 W-X8) to afford the title compound (266 mg, 84%): ^{1}H NMR (360 MHz,

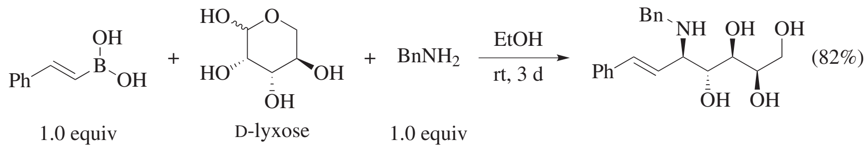
DMSO-d_6) δ7.8–7.0 (m, 15H), 4.78 (s, 1H), 4.17 (s, 1H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 172.8, 142.4, 133.6, 129.6, 128.1, 127.5, 127.1, 126.9, 126.7, 63.6, 62.2. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41; Found: C, 79.48; H, 6.17; N, 4.32.



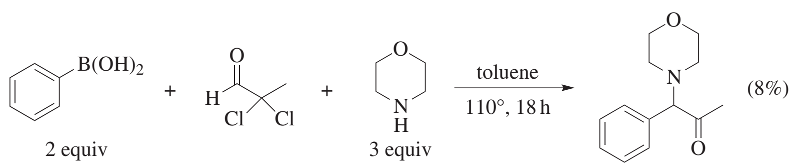
(2*R*,3*E*)-2-[[(1*S*)-2-Hydroxy-1-phenylethyl]amino]-4-phenyl-3-butenoic Acid [Preparation of α-Vinylglycine Derivatives from Glyoxylic Acid].[33] To a stirred solution of glyoxylic acid monohydrate (291 mg, 3.16 mmol) in CH_2Cl_2 (14 mL) was added (*S*)-2-phenylglycinol (434 mg, 3.16 mmol) in one portion, followed by (*E*)-β-styrenylboronic acid (469 mg, 3.17 mmol). The reaction mixture was stirred vigorously at rt for 12 h. The precipitate was isolated by filtration and washed with cold CH_2Cl_2 (15 mL). The crude material gave good spectroscopic data, while ^{1}H NMR analysis indicated a dr of >99:1. Recrystallization from H_2O/*t*-BuOH afforded an analytically pure title compound (733 mg, 78%, dr >99:1): ^{1}H NMR (360 MHz, DMSO-d_6) δ 7.50–7.20 (m, 10H), 6.54 (d, $J = 15.2$ Hz, 1H), 6.20 (dd, $J = 15.2$, 7.3 Hz, 1H), 3.84 (m, 1H), 3.64 (d, $J = 7.3$ Hz, 1H), 3.45 (m, 2H); ^{13}C NMR (90 MHz, DMSO-d_6) δ 172.8, 139.8, 136.2, 131.1, 128.6, 128.3, 127.7, 127.5, 126.9, 126.4, 126.3, 66.0, 63.0, 61.0; HRMS-CI (m/z): $[M + H]^+$ calcd for $C_{18}H_{20}NO_3$, 298.1365; found, 298.1449. Anal. Calcd for $C_{18}H_{20}NO_3$: C, 72.71; H, 6.44; N, 4.71; Found: C, 72.27; H, 6.41; N, 4.69.



(±)-2,3-*anti*-3-*N*,*N*-Dibenzylamino-5-phenyl-4-penten-2-ol [Preparation of *anti*-1,2-Amino Alcohols from α-Hydroxy Aldehydes].[39] To a solution of racemic 2-hydroxypropanal (130 mg, 1.76 mmol) in EtOH (7 mL) were added (*E*)-β-styrenylboronic acid (260 mg, 1.76 mmol) and dibenzylamine (347 mg, 1.76 mmol). The flask was sealed and the reaction mixture was stirred at rt for 24 h. The volatiles were then removed and the residue was purified by column chromatography on silica gel using hexanes/EtOAc (8:3) as eluent to give the title compound as a colorless oil (560 mg, 89%, dr >99:1): ^{1}H NMR (360 MHz, C_6D_6) δ 7.45–7.05 (m, 15H), 6.38 (d, $J = 16.0$ Hz, 1H), 6.19 (dd, $J = 16.0$ Hz, 9.6 Hz, 1H), 3.90 (m, 1H), 3.82 (d, $J = 13.8$ Hz, 2H), 3.34 (d, $J = 13.8$ Hz, 2H), 3.00 (dd, $J = 9.6$ Hz, 7.0 Hz, 1H), 1.27 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 139.7, 136.7, 136.4, 128.7, 128.6, 128.3, 127.9, 126.9, 126.5, 124.8, 68.5, 67.8, 55.1, 20.4; HRMS-EI (m/z): $[M + H]^+$ calcd for $C_{25}H_{28}NO$, 358.2093; found, 358.2099.

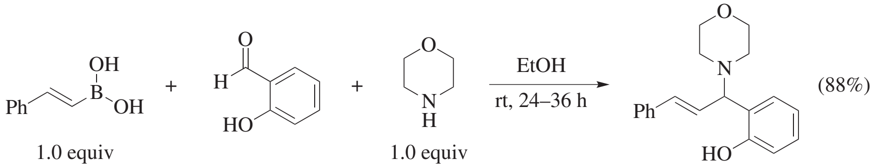


(2*R*,3*R*,4*R*,5*R*,*E*)-5-Benzylamino-7-phenyl-6-heptene-1,2,3,4-tetraol [Preparation of *anti*-1,2-Amino Alcohols from Sugars].[69] To a solution of D-lyxose (200 mg, 1.33 mmol) in EtOH (2 mL) was added benzylamine (0.146 mL, 143 mg, 1.33 mmol) and (*E*)-β-styrenylboronic acid (197 mg, 1.33 mmol). After the mixture was stirred at rt for 3 d, the solvent was removed in vacuo. Purification of the crude product by silica gel column chromatography (EtOAc/MeOH, gradient 100:0 to 4:1) gave the product as a brown foamy solid in 82% yield (376 mg). A small amount was repurified to give a white solid for analysis: mp 114–116°; R_f 0.22 (EtOAc/MeOH/NH_3, 8:1:1); $[\alpha]_D^{24} - 45.8$ (*c* 0.95, MeOH); IR 3355, 3283, 2909, 2848, 2356, 1491, 1347, 1019 cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD) δ 7.45 (d, $J = 8$ Hz, 2H), 7.32 (m, 6H), 7.23 (m, 2H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.22 (dd, $J = 16.0$ Hz, 9.0 Hz, 1H), 3.88 (d, $J = 13.0$ Hz, 1H), 3.87 (d, $J = 7.0$ Hz, 1H), 3.80 (ddd, $J = 9.0$ Hz, 5.0 Hz, 2 Hz, 1H), 3.69 (d, $J = 13.0$ Hz, 1H), 3.60 (d, $J = 6.5$ Hz, 2H), 3.53 (apparent br d, $J = 9.0$ Hz, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 140.6, 138.4, 135.6, 129.7, 129.6, 129.5, 128.6, 128.4, 128.2, 127.5, 74.1, 72.8, 71.8, 64.8, 64.3, 51.6; LRMS-ESI (m/z): $[M + H]^+$ 343.8 (100%); HRMS-ESI (m/z): $[M + H]^+$ calcd for $C_{20}H_{26}NO_4$, 344.1862; found, 344.1867.

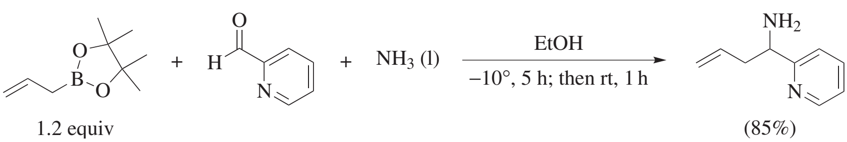


1-Morpholino-1-phenyl-2-propanone [Preparation of α-Amino Ketones from α,α-Dichloroaldehydes].[46] To a stirred solution of 2,2-dichloropropanal (508 mg, 4.0 mmol) in anhydrous toluene (18 mL) was added morpholine (1.04 g, 12 mmol) in one portion, followed by phenylboronic acid (975 mg, 8.0 mmol). The mixture was stirred at 110° (toluene, reflux) for 18 h, after which it was cooled to 0° and filtered. The filtrate was subjected to an acid/base extraction: 2 M HCl (18 mL) was added and the aqueous phase was washed with Et_2O (18 mL, 10 mL, 5 mL); then 3 M NaOH (18 mL) was added to the aqueous phase and the resulting solution was extracted with CH_2Cl_2 (18 mL, 10 mL, 5 mL, 5 mL). The combined CH_2Cl_2 fractions were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting brown oil (885 mg, 50%) was purified by silica gel chromatography to afford the product as a yellow oil (132 mg, 8%): R_f 0.18 (hexane/EtOAc, 7:3); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.49–7.29 (m, 5H), 3.91 (s, 1H), 3.75 (t, $J = 4.6$ Hz, 4H), 2.47–2.35 (m, 4H), 2.11 (s, 3H); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 206.6, 134.6, 129.1, 128.9, 128.6, 82.3, 66.8, 52.0, 26.4.

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.00; H, 7.85; N, 6.31.

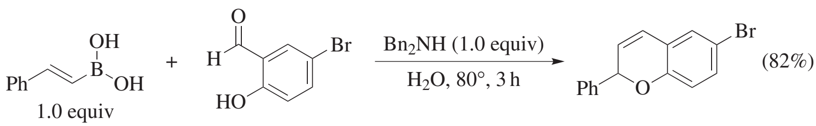


(*E*)-2-(1-Morpholino-3-phenylallyl)phenol [Preparation of 2-Hydroxybenzylamines from Salicylaldehydes].[14] To a mixture of salicylaldehyde (122 mg, 1.0 mmol) and morpholine (87 mg, 1.0 mmol) in EtOH (10 mL) was added (*E*)-β-styrenylboronic acid (148 mg, 1.0 mmol). The solution was stirred at rt while being monitored by TLC (EtOAc/hexane, 10:1). After completion of the reaction (24 h) the solvent was evaporated and the product was isolated by silica gel chromatography using EtOAc/hexane (10:1) to afford the product (260 mg, 88%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.44–6.65 (m, 9H), 6.55 (d, $J = 15.8$ Hz, 1H), 6.29 (dd, $J = 15.6$ Hz, 9.5 Hz, 1H), 3.99 (d, $J = 9.3$ Hz, 1H), 3.74 (br m, 4H), 2.59 (br m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 156.3, 136.0, 133.9, 128.9, 128.6, 128.5, 128.0, 126.5, 125.9, 123.9, 119.7, 116.6, 74.0, 66.8, 51.1; HRMS-CI (m/z): [M + H^+] calcd for $C_{19}H_{22}NO_2$, 296.1572; found 296.1648.

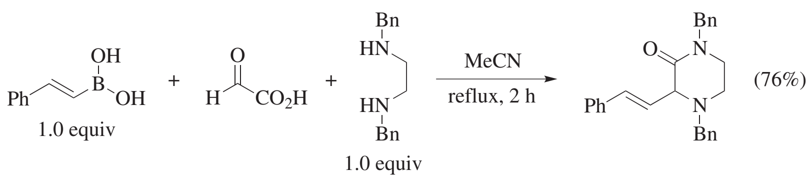


1-(2-Pyridinyl)-3-buten-1-amine [Preparation of Aminomethylarenes from Aromatic Aldehydes].[28] To a dry, two-neck flask with an argon balloon and a rubber septum cooled at −78°, gaseous ammonia was introduced through a needle to obtain liquid ammonia (ca. 0.5 mL). After addition of EtOH (0.5 mL), picolinaldehyde (54 mg, 0.5 mmol) was added to the ammonia solution at −78° and transfer was completed with an EtOH (0.5 mL) rinse. The mixture was warmed to −10° and was stirred at that temperature for 2 h. During that time, excess ammonia had vaporized into the balloon. Pinacol allylboronate (101 mg, 0.6 mmol) in EtOH (0.5 mL) was then added dropwise to the solution, which caused a colorless precipitate to form. The mixture was stirred at −10° for 3 h and at rt for 1 h. The balloon and the septum were then removed to vaporize most of the ammonia, and 1 N aqueous HCl was added to acidify the solution (pH ca. 1). The mixture was washed with Et_2O (3×), alkalized with 6 N aqueous NaOH (pH ca. 10), and extracted with CH_2Cl_2 (3×). The combined CH_2Cl_2 layers were dried (Na_2CO_3), filtered, and evaporated to give the almost pure amine product, which was purified by preparative TLC (hexane/isopropylamine, 10:1) to give the title product in 85% yield (63 mg): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (ddd, $J = 4.9$ Hz, 1.8 Hz, 1.1 Hz, 1H), 7.65 (ddd, $J = 7.9$ Hz, 7.5 Hz, 1.8 Hz,

1H), 7.31 (d, J = 7.9 Hz, 1H), 7.16 (ddd, J = 7.5 Hz, 4.9 Hz, 1.1 Hz, 1H), 5.77 (dddd, J = 17.0 Hz, 10.2 Hz, 7.9 Hz, 6.4 Hz, 1H), 5.16–5.06 (m, 2H), 4.06 (dd, J = 7.9 Hz, 5.3 Hz, 1H), 2.60 (dddt, J = 13.7 Hz, 6.4 Hz, 5.3 Hz, 1.4 Hz, 1H), 2.41 (dddt, J = 13.7 Hz, 7.9 Hz, 7.9 Hz, 1.0 Hz, 1H), 1.88 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 149.1, 136.4, 135.1, 121.9, 120.9, 117.7, 56.5, 43.2; HRMS-ESI (m/z): [M + H^+] calcd for $C_9H_{13}N_2$, 149.1079; found, 149.1080.

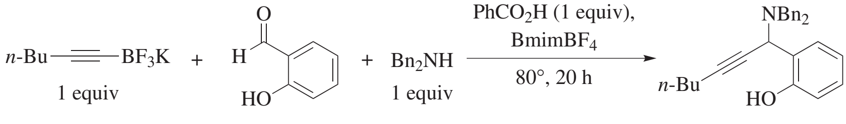


6-Bromo-2-phenyl-2*H*-chromene [Preparation of 2*H*-Chromenes from Salicylaldehydes].[55] A mixture of either (E)-β-styrenylboronic acid (148 mg, 1.0 mmol) or potassium (E)-β-styrenyltrifluoroborate (210 mg, 1.0 mmol) with 5-bromosalicylaldehyde (201 mg, 1.0 mmol) and dibenzylamine (197 mg, 1.0 mmol) in 2 mL of water was stirred at 80° for 3 h. The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL), dried (Na_2SO_4), filtered, and concentrated. The yellow syrupy residue was purified by column chromatography (CH_2Cl_2/hexane, 5:1). The title product (R_f 0.4) was eluted, and the mixture was left on solvent-wet silica until the purple-colored band faded completely, and more product was eluted with CH_2Cl_2, affording 235 mg (82%) of the product as a viscous yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.42 (m, 5H); 7.30 (dd, J = 8.6 Hz, 2.3 Hz, 1H), 7.24 (d, J = 2.3 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H), 6.55 (dd, J = 9.9 Hz, 1.1 Hz, 1H), 6.04–6.00 (m, 1H), 5.93 (dd, J = 9.9 Hz, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 140.1, 131.9, 129.0, 128.7, 128.5, 127.0, 125.9, 123.1, 122.9, 117.7, 113.0, 77.2.

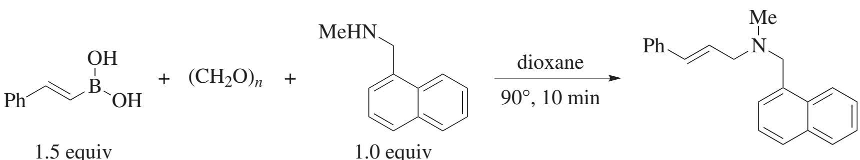


1,4-Dibenzyl-3-((*E*)-2-phenylethenyl)-2-piperazinone [Preparation of 2-Piperazinones from 1,2-Diamines].[62] To a mixture of N,N-dibenzylethylenediamine (240 mg, 1.0 mmol) and glyoxylic acid monohydrate (92 mg, 1.0 mmol) in CH_3CN (20 mL) was added (E)-β-styrenylboronic acid (144 mg, 1.0 mmol). The solution was heated at reflux and was monitored by TLC (hexanes/EtOAc, 3:2). After 2 h, the solvent was evaporated and the product was isolated by silica gel chromatography using hexanes/EtOAc (7:3) to afford the title compound (291 mg, 76%): ^{1}H NMR (250 MHz, CD_3OD) δ 7.48–7.20 (m, 15H), 6.76 (d, J = 15.9 Hz, 1H), 6.33 (dd, J = 15.9 Hz, 7.9 Hz, 1H), 4.64 (dd, J = 17.5 Hz, 4.7 Hz, 1H), 3.92 (d, J = 13.3 Hz, 1H), 3.86 (d, J = 7.9 Hz, 1H), 3.43 (d, J = 13.3 Hz, 1H), 3.23 (t, J = 5.2 Hz, 2H), 3.02 (m, 1H), 2.54

(m, 1H); ^{13}C NMR (62.5 MHz, CD_3OD) δ 170.5, 139.0, 137.9, 137.87, 137.1, 130.1, 129.8, 129.7, 129.5, 129.1, 129.0, 128.7, 128.4, 127.6, 126.3, 69.2, 59.4, 51.2, 46.8, 46.5; HRMS (m/z): $[M + H]^+$ calcd for $C_{26}H_{27}N_2O^+$, 383.2045; found, 383.2127.



2-[1-[bis(Phenylmethyl)amino]-2-heptyn-1-yl]phenol [Preparation of Propargylic Amines in an Ionic Liquid].[63] To a mixture of salicylaldehyde (1 mmol) and dibenzylamine (1 mmol) in 1-butyl-3-methylimidazolium tetrafluoroborate (800 mg), were added potassium 1-hexynyltrifluoroborate[87] (1 mmol) and benzoic acid (1 mmol). The mixture was stirred at 80° for 20 h, the product was extracted into Et_2O (3 × 5 mL), the solvent was removed, and the crude product was purified by silica gel column chromatography to give the title compound in 81% yield (311 mg):^{1}H NMR ($CDCl_3$) δ 7.60 (d, $J = 8$ Hz, 1H), 7.40–6.80 (m, 13H), 4.95 (br s, 1H), 3.78 (d, $J = 13$ Hz, 2H), 3.48 (d, $J = 13$ Hz, 2H), 2.50 (m, 2H), 1.80–1.55 (m, 4H), 1.0 (t, $J = 7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 156.5, 137.2, 129.7, 129.2, 128.9, 128.6, 127.7, 122.4, 119.2, 116.2, 90.9, 72.1, 54.7, 54.5, 31.1, 22.1, 18.5, 13.6. Anal. Calcd for $C_{27}H_{29}NO$: C, 84.55; H, 7.62; N, 3.65. Found: C, 84.33; H, 7.67; N, 3.53.



(2*E*)-*N*-Methyl-*N*-(1-naphthylmethyl)-3-phenyl-2-propen-1-amine (Naftifine) [Preparation of Allylic Amines from Alkenylboronic Acids].[7] A slurry of *N*-methyl-*N*-1-naphthylmethylamine (67 mg, 0.39 mmol) and paraformaldehyde (12 mg, 0.39 mmol) in dioxane (1 mL) was heated to 90°. After 10 min, the solution became clear and TLC analysis indicated consumption of the amine. To this cooled solution were added (*E*)-β-styrenylboronic acid (87 mg, 0.58 mmol) and more dioxane (1 mL), and the mixture was heated for 10 min at 90°. Upon cooling, the mixture was acidified with 2 N HCI and washed with Et_2O (3×). Addition of 3 N NaOH to bring the pH to 14, followed by extraction with Et_2O, drying of the Et_2O layer over Na_2SO_4, filtration, and removal of the solvents gave pure naftifine as a yellow viscous liquid (81 mg, 82%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.38–8.35 (m, 1H), 7.91–7.80 (m, 2H), 7.58–7.26 (m, 9H), 6.63 (d, $J = 15.9$ Hz, 1H), 6.43 (dt, $J = 15.8$, 6.5 Hz, 1H), 3.99 (s, 2H), 3.32 (d, $J = 6.5$ Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 137.06,

134.82, 133.82, 132.80, 132.42, 128.49, 128.38, 127.88, 127.55, 127.39, 127.31, 126.25, 125.83, 125.52, 125.05, 124.58, 60.35, 60.06, 42.42; MS-EI *m/z* (relative intensity) 287.30 (39), 196.30 (37), 141.30 (100), 117.30 (31), 115.30 (51).

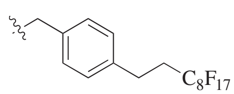
TABULAR SURVEY

Reactions have been classified on the basis of the types of products that are formed and cover the literature from 1993 to 2011. Supplemental references are provided in the bibliography for reactions reported in 2012, and in 2013 up to the end of April 2013.

Within each table, entries are organized in the order of increasing number of carbons (not including protecting groups) in the amine or the carbonyl component. In Tables 1, 2A, and 7E, glyoxylic acid is a non-illustrated coreactant in all reactions. A note at the top of every page reminds the reader of this fact. Likewise, in Table 2B, ethyl glyoxalate is a co-reactant, and in Table 2C, 2-oxopropanoic acid is a coreactant.

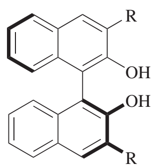
Unreported yields are indicated with the notation "(—)".

The following abbreviations, excluding those found in "*The Journal of Organic Chemistry* Standard Abbreviations and Acronyms," are used in the text and the Tables.

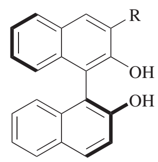
AD-mix-α	osmium-catalyzed asymmetric dihydroxylation using a commercially available mixture containing (dihydroquinine)-phthalazine [$(DHQ)_2$–PHAL] as the chiral ligand
$BdmimBF_4$	1-butyl-2,3-dimethylimidazolium tetrafluoroborate
$BmimBF_4$	1-butyl-3-methylimidazolium tetrafluoroborate
CTAB	cetyltrimethylammonium bromide
Cy	cyclohexyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DBSA	dodecylbenzenesulfonic acid
DDMAPS	*N*-dodecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate
deguPHOS	(3*R*,4*R*)-3,4-bis(diphenylphosphino)-1-(phenylmethyl)-pyrrolidine
ELS	evaporative light scattering
ELSD	evaporative light-scattering detector
$EmimBF_4$	1-ethyl-3-methylimidazolium tetrafluoroborate
f-Bn	
F-SPE	fluorous solid-phase extraction
HFIP	hexafluoroisopropyl alcohol

LC	liquid chromatography
LC-UV/ELS	liquid chromatography with ultraviolet and ELS detection
MS	mass spectrometry; molecular sieves
MW	microwave irradiation
Np	naphthyl
PMP	4-methoxyphenyl
SDBS	sodium dodecylbenzenesulfonate
SDS	sodium dodecyl sulfate
TMP	2,2,6,6-tetramethylpiperidine
Tol	tolyl

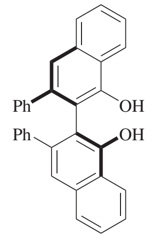
CHART 1. CATALYSTS USED IN TABLE 2B, TABLE 3, AND TABLE 7D



	R
1a	H
1b	Br
1c	Ph
1d	3,5-$Me_2C_6H_3$
1e	SO_2CF_3
1f	3,5-$(CF_3)_2C_6H_3$



	R
2a	Br
2b	Ph
2c	SO_2CF_3



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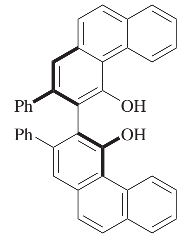
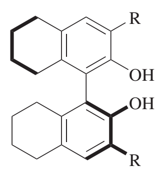
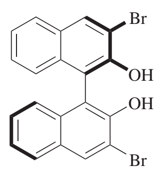


4 (*S*)-VAPOL

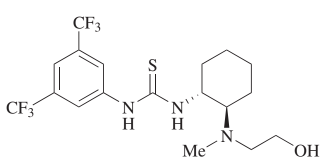


	R
5a	Br
5b	3,5-$Me_2C_6H_3$

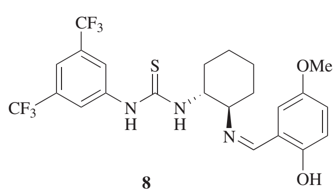


6

CHART 2. CATALYSTS USED IN TABLE 10



7



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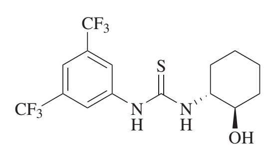

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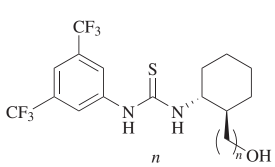
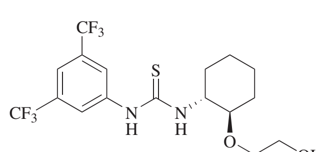


	n
10a	1
10b	2
10c	3



11

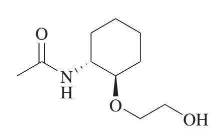


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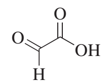
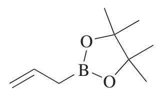
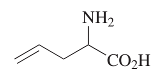
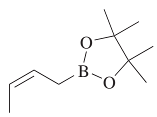
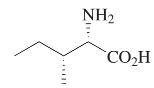
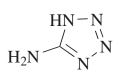
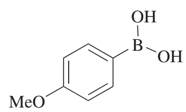
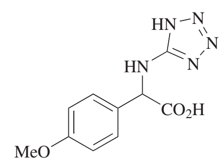
TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS

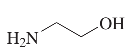
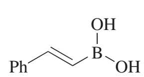
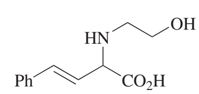
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.



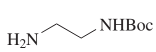
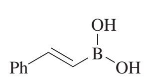
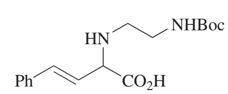
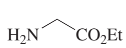
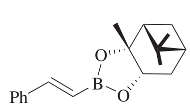
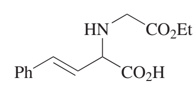
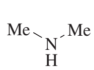
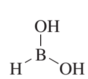
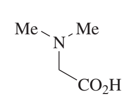
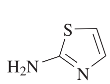
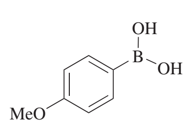
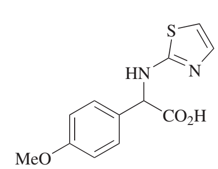
glyoxylic acid

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_0				
NH_3 (25% aq)		1. Glyoxylic acid, NH_3, EtOH, rt, 30 min 2. Boronate, rt, 3 h	 (quant)	28
NH_3		1. Boronate, NH_3, EtOH, –78°; then –10°, 30 min 2. Glyoxylic acid, –10°, 3 h 3. H_2, Pd/C, rt, 12 h	 major (*rac*) (91) dr >99.5:0.5	28
C_1				
		MeCN/DMF (10:1)		22

	Temp (°)	Time	
MW, 300W	120	5–10 min	(54)
—	82	0.5–4 h	(54)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
		See table.		

Solvent	Temp	Time (h)		Refs.
EtOH	rt	12–48	(82)	33
H_2O	80°	24	(67)	56

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeOH or CH_2Cl_2, rt	 (88)	88
		CH_2Cl_2, rt	 (0)	37
		CH_2Cl_2, rt, 48 h	 (42)[a]	25, 26
C_3				
		MeCN/DMF (10:1)		22

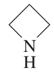
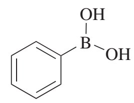
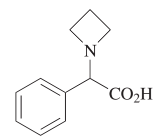
	Temp (°)	Time	
MW, 300 W	120	5–10 min	(49)
—	82	0.5–4 h	(49)

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

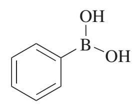
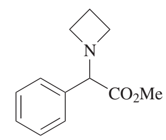
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

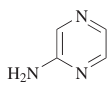
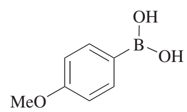
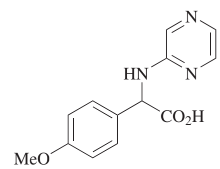
C_3

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		Solvent(s), rt, 20 h		18

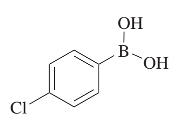
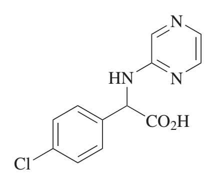
Solvent(s)		Conv (%)
CH_2Cl_2/HFIP (9:1)	(—)	59
CH_2Cl_2	(—)	42

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CH_2Cl_2/HFIP (9:1), rt, 45 h 2. $TMSCHN_2$	 (63)[b]	18

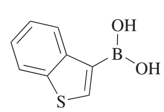
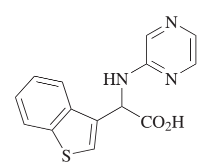
C_4

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN/DMF (10:1)		22

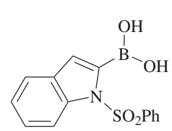
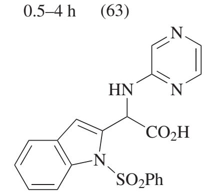
	Temp (°)	Time	
MW, 300 W	120	5–10 min	(90)
—	82	0.5–4 h	(90)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN/DMF (10:1)		22

	Temp (°)	Time	
MW, 300 W	120	5–10 min	(<5)
—	82	0.5–4 h	(<5)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN/DMF (10:1)		22

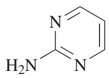
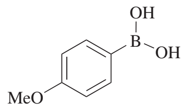
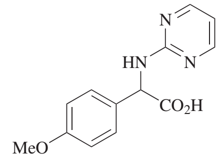
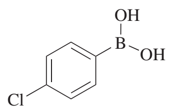
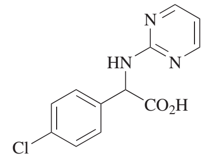
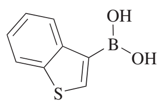
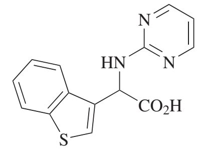
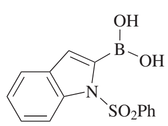
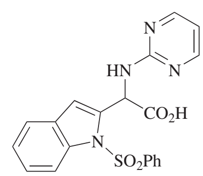
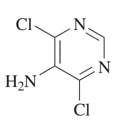
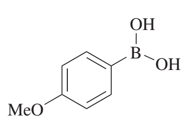
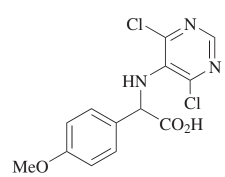
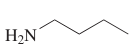
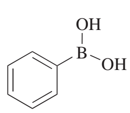
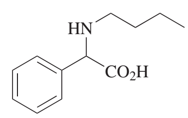
	Temp (°)	Time	
MW, 300 W	120	5–10 min	(63)
—	82	0.5–4 h	(63)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN/DMF (10:1)		22

	Temp (°)	Time	
MW, 300 W	120	5–10 min	(85)
—	82	0.5–4 h	(85)

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		MeCN/DMF (10:1)		22
		MeCN/DMF (10:1)		22
		MeCN/DMF (10:1)		22
		MeCN/DMF (10:1)		22
		MeCN/DMF (10:1)		22
		Solvent(s), rt, 20 h		18

Conditions for product 3:

	Temp (°)	Time	
MW, 300 W	120	5–10 min	(86)
—	82	0.5–4 h	(86)

Conditions for product 5:

	Temp (°)	Time	
MW, 300 W	120	5–10 min	(12)
—	82	0.5–4 h	(12)

Conditions for product 7:

	Temp (°)	Time	
MW, 300 W	120	5–10 min	(36)
—	82	0.5–4 h	(17)

Conditions for product 9:

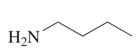
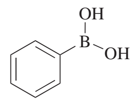
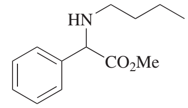
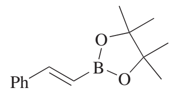
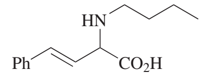
	Temp (°)	Time	
MW, 300 W	120	5–10 min	(70)
—	82	0.5–4 h	(70)

Conditions for product 12:

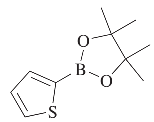
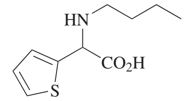
	Temp (°)	Time	
MW, 300 W	120	5–10 min	(17)
—	82	0.5–4 h	(17)

Conditions for product 15:

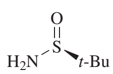
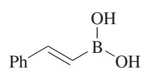
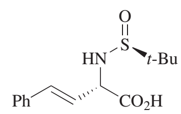
Solvent(s)		Conv (%)
CH_2Cl_2/HFIP (9:1)	(—)	7
CH_2Cl_2	(—)	0

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_4 		1. CH_2Cl_2/HFIP (9:1), rt, 45 h 2. $TMSCHN_2$	 (—) 7% conv[b]	18
		Solvent, rt		21

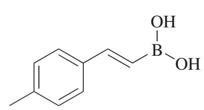
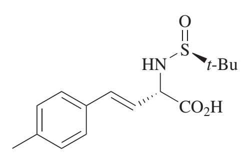
Solvent	Time (h)	
MeOH	72	(66)
HFIP	4	(77)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		Solvent, rt		21

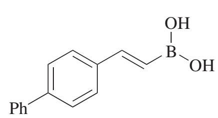
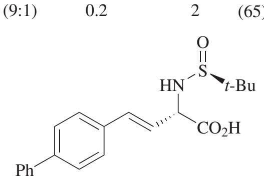
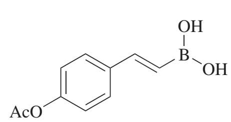
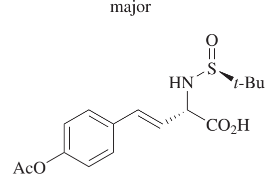
Solvent	Time (h)	
MeOH	72	(68)
HFIP	4	(83)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		Solvent(s), rt	 major dr 10:1	89

Solvent(s)	[Reactants] (M)	Time (h)	
CH_2Cl_2	0.2	48	(55)
CH_2Cl_2	0.33	12	(94)
CH_2Cl_2/HFIP (9:1)	0.2	2	(65)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		Solvent(s), rt	 major dr 20:1	89

Solvent(s)	[Reactants] (M)	Time (h)	
CH_2Cl_2	0.2	48	(55)
CH_2Cl_2	0.33	12	(99)
CH_2Cl_2/HFIP (9:1)	0.2	2	(65)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		[Reactants] = 0.33 M, CH_2Cl_2, rt, 12 h	 major (90) dr 20:1	89
		[Reactants] = 0.33 M, CH_2Cl_2, rt, 12 h	 major (99) dr 18:1	89

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

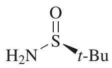
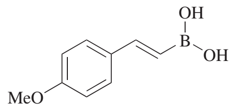
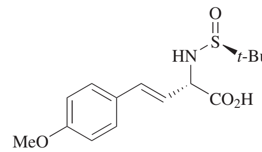
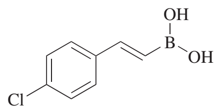
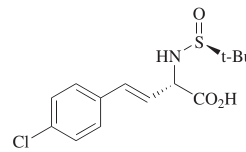
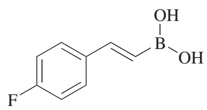
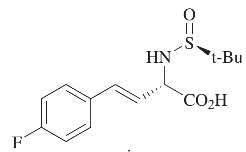
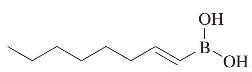
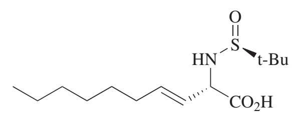
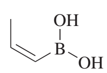
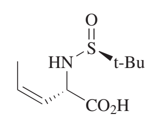
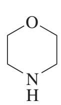
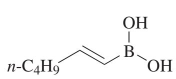
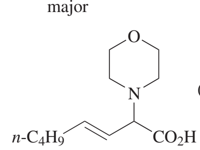
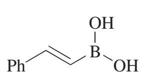
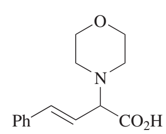
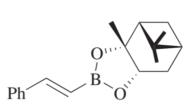
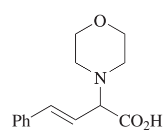
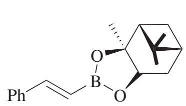
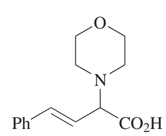
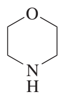
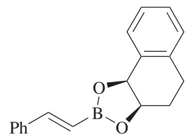
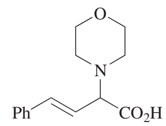
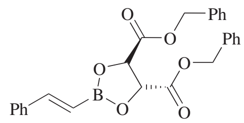
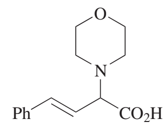
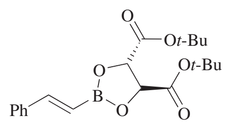
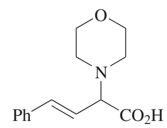
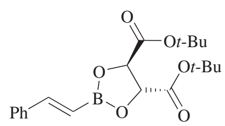
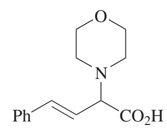
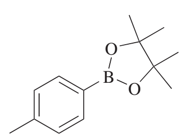
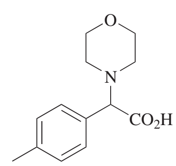
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		[Reactants] = 0.33 M, CH_2Cl_2, rt, 12 h	 major (99) dr >20:1	89
		[Reactants] = 0.33 M, CH_2Cl_2, rt, 12 h	 major (95) dr 13:1	89
		[Reactants] = 0.33 M, CH_2Cl_2, rt, 12 h	 major (90) dr >20:1	89
		[Reactants] = 0.33 M, CH_2Cl_2, rt, 12 h	 major (83) dr 85:15	89
		[Reactants] = 0.33 M, CH_2Cl_2, rt, 12 h	 major (85) dr 89:11	89
		EtOH, 50°, 12–48 h	 (78)	33
		H_2O, 50°, 24 h	 (75)	56
		CH_2Cl_2, rt	 (78) er 57.6:42.4	37
		CH_2Cl_2, rt	 (81) er 57.6:42.4	37

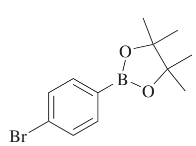
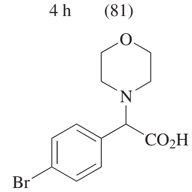
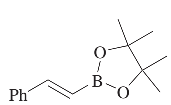
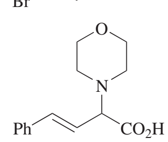
TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

C_4

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt	 (78) er 55.5:44.5	37
		CH_2Cl_2, rt	 (59) er 55.2:44.8	37
		CH_2Cl_2, rt	 (71) er 53.4:46.6	37
		CH_2Cl_2, rt	 (80) er 53.2:46.8	37
		See table.		

	Solvent	Temp	Time		Refs.
—	CH_2Cl_2	rt	—	(12)	19
MW, 300W	MeOH	120°	10 min	(21)	21
—	HFIP	rt	4 h	(81)	21

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt	 (5)	19
		See table.		

	Solvent	Temp	Time		Refs.
—	CH_2Cl_2	rt	—	(82)	19
MW, 300W	MeOH	120°	10 min	(85)	21
—	HFIP	rt	4 h	(97)	21

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

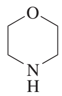
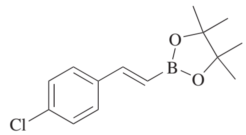
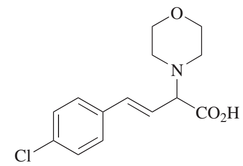
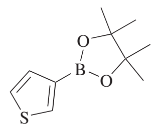
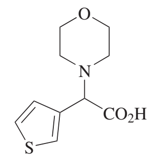
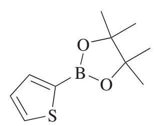
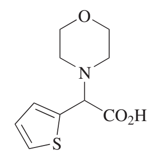
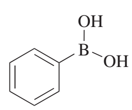
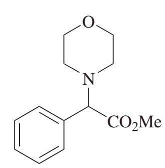
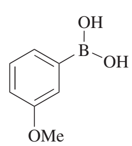
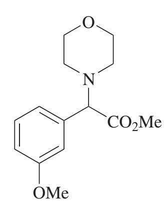
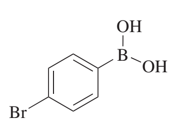
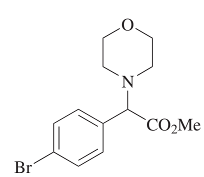
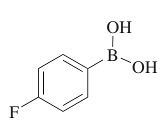
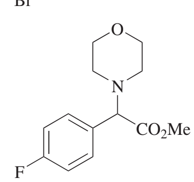
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CH_2Cl_2, rt	 (71)	19
		See table.		
		Solvent / Temp / Time		
		— / CH_2Cl_2 / rt / —	(12)	19
		MW, 300W / MeOH / 120° / 10 min	(21)	21
		— / HFIP / rt / 4 h	(81)	21
		MW, 300W / HFIP / 120° / 10 min	(94)	21
		See table.		21
		Solvent / Temp / Time		
		MW, 300W / MeOH / 120° / 10 min	(92)	
		— / HFIP / rt / 4 h	(89)	
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, rt, 3 h	 (40)	50
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, rt, 3 h	 (42)	50
		1. CH_2Cl_2,MW, 120°, 10 min 2. $TMSCHN_2$, THF, rt, 3 h	 (35)	50
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, rt, 3 h	 (34)	50

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

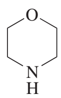
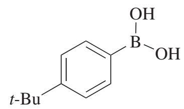
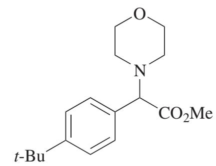
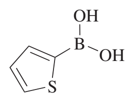
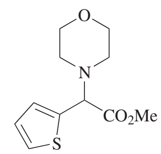
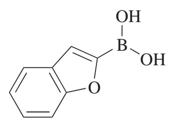
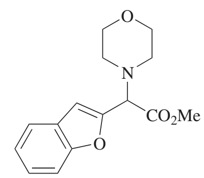
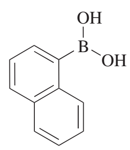
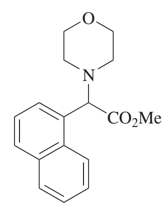
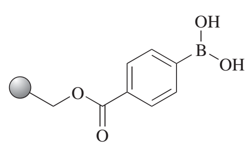
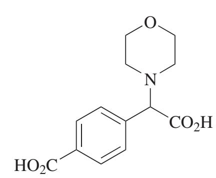
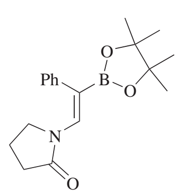
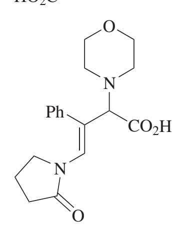
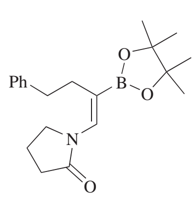
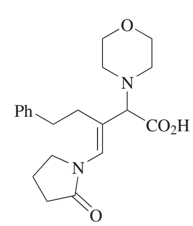
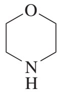
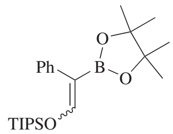
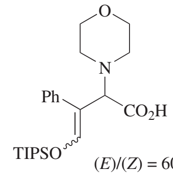
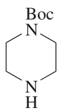
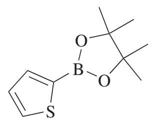
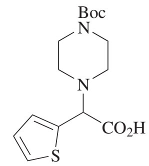
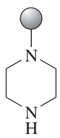
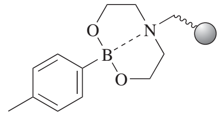
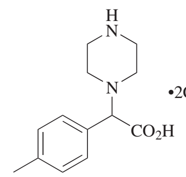
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, rt, 3 h	 (31)	50
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, rt, 3 h	 (62)	50
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, rt, 3 h	 (10)	50
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, rt, 3 h	 (65)	50
		1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •CF_3CO_2H (26)[c] >95% pure	13
		HFIP, 50°, 24 h	 (97)	90
		HFIP, rt, 24 h	 (92)	90

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	 (*E*)/(*Z*) = 40:60	HFIP, rt, 24 h	 (*E*)/(*Z*) = 60:40 (74)	90
		See table.		21

	Solvent	Temp	Time	
MW, 300W	MeOH	120°	10 min	(89)
—	HFIP	rt	4 h	(86)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. Solvents, 65°, 24 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 $\bullet 2CF_3CO_2H$	32

Solvents		Conv (%)
DMF/EtOH (7:1)	(—)	65
DMF/*n*-BuOH (7:1)	(—)	54
dioxane/*n*-BuOH (7:1)	(—)	23
THF/$(HOCH_2)_2$ (7:1)	(—)	37
THF/EtOH (7:1)	(—)	79

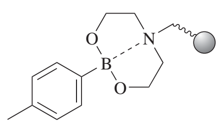
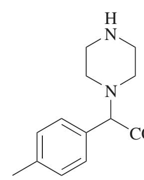
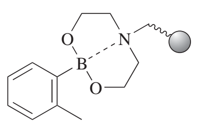
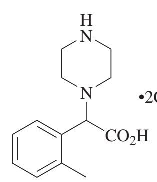
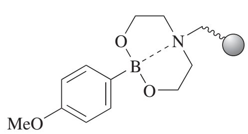
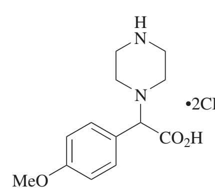
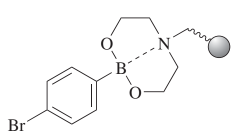
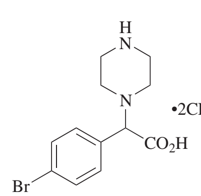
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. THF/EtOH (8:3), 65°, 24–48 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 $\bullet 2CF_3CO_2H$ (85)[d]	32, 91
		1. THF/EtOH (8:3), 65°, 24–48 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 $\bullet 2CF_3CO_2H$ (73)[d]	32, 91
		1. THF/EtOH (8:3), 65°, 24–48 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 $\bullet 2CF_3CO_2H$ (>95)[d]	32, 91
		1. THF/EtOH (8:3), 65°, 24–48 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 $\bullet 2CF_3CO_2H$ (10)[d]	32, 91

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

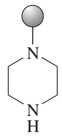
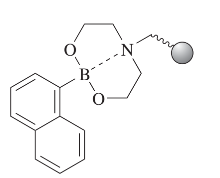
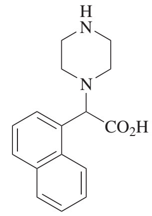
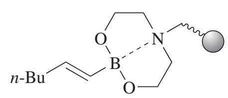
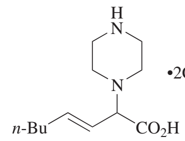
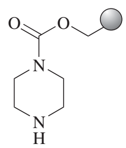
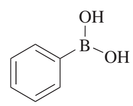
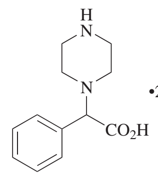
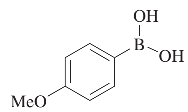
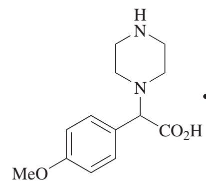
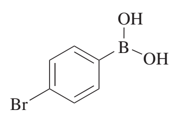
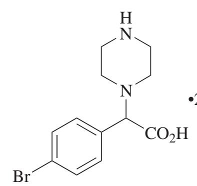
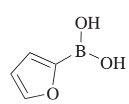
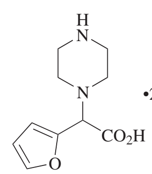
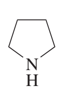
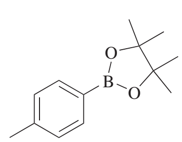
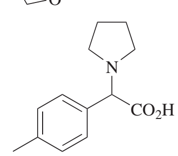
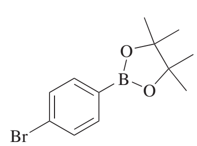
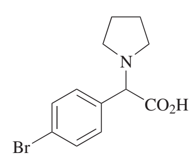
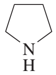
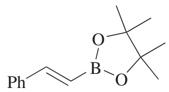
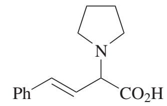
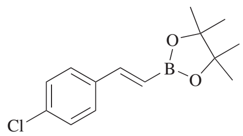
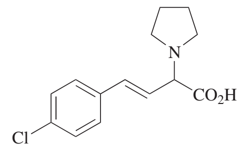
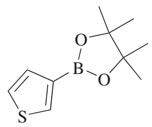
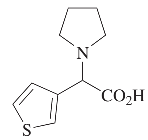
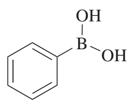
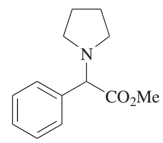
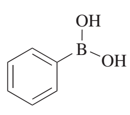
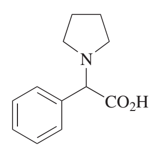
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_4				
		1. THF/EtOH (8:3), 65°, 24–48 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 •$2CF_3CO_2H$ (90)[d]	32, 91
		1. THF/EtOH (8:3), 65°, 24–48 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 •$2CF_3CO_2H$ (>95)[d]	32, 91
		1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •$2CF_3CO_2H$ (81)[e] >95% pure	13
		1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •$2CF_3CO_2H$ (42)[e] >95% pure	13
		1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •$2CF_3CO_2H$ (78)[e] >95% pure	13
		1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •$2CF_3CO_2H$ (24)[e] 70% pure	13
		CH_2Cl_2, rt	 (9)	19
		CH_2Cl_2, rt	 (5)	19

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

C_4

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt	 (75)[f]	19
		CH_2Cl_2, rt	 (70)[f]	19
		CH_2Cl_2, rt	 (28)	19
		1. CH_2Cl_2/HFIP (9:1), rt, 45 h 2. $TMSCHN_2$	 (78)[b]	18
		Solvent(s), rt, 20 h		18

Solvent(s)		Conv (%)
CH_2Cl_2/HFIP (9:1)	(—)	86
CH_2Cl_2	(—)	25

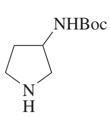
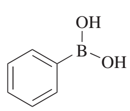
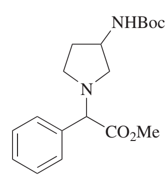
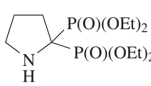
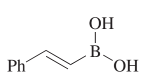
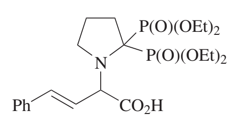
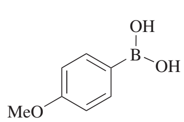
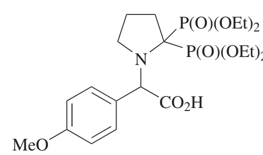
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CH_2Cl_2/HFIP (9:1), rt, 24 h 2. $TMSCHN_2$	 (80)[g] dr 50:50	18
		EtOAc, reflux, 3.5–4 h	 (47)	92
		EtOAc, reflux, 3.5–4 h	 (65)	92

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

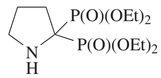
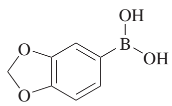
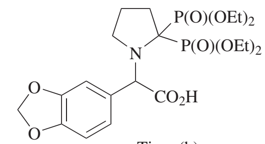
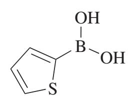
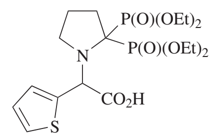
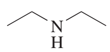
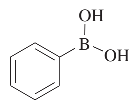
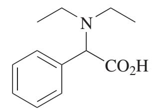
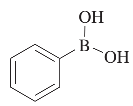
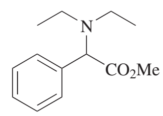
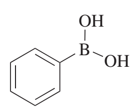
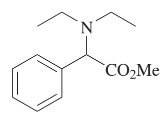
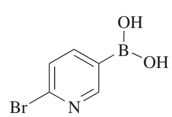
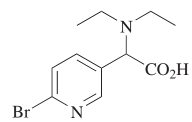
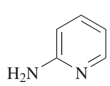
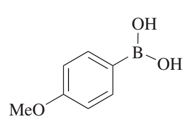
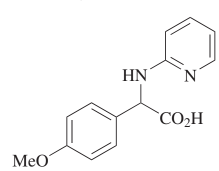
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_4				
		EtOAc, reflux	 (73)	
			Time (h): 3.5–4	92
			Time (h): 2–2.5	93
		EtOAc, reflux, 3.5–4 h	 (80)	92
		Solvent(s), rt, 92 h		18
		Solvent(s): CH_2Cl_2/HFIP (9:1)	(—) Conv (%): 26	
		Solvent(s): CH_2Cl_2	(—) Conv (%): 0	
		1. CH_2Cl_2/HFIP (9:1), rt, 45 h 2. $TMSCHN_2$	 (—), 11% conv[b]	18
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, 3 h	 (18), 54% conv	50
		CH_2Cl_2, rt, 24 h	 (0)	27
C_5				
		MeCN/DMF (10:1)		22
		MW, 300 W; Temp (°) 120; Time 5–10 min	(94)	
		—; Temp (°) 82; Time 0.5–4 h	(94)	

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

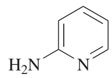
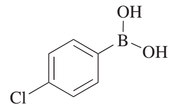
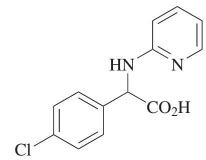
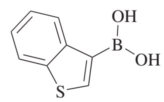
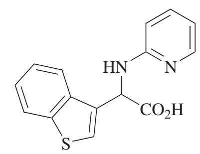
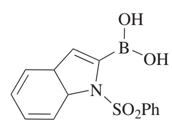
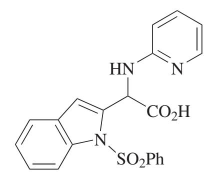
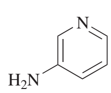
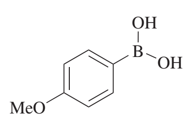
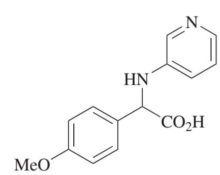
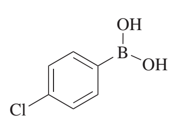
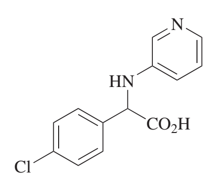
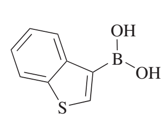
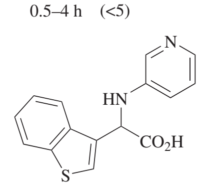
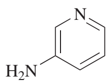
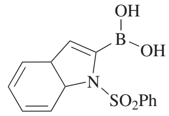
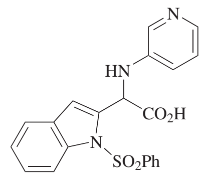
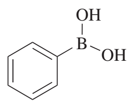
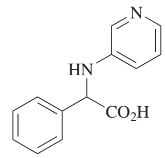
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_5				
		MeCN/DMF (10:1)	 Temp (°) Time MW, 300 W 120 5–10 min (<5) — 82 0.5–4 h (<5)	22
		MeCN/DMF (10:1)	 Temp (°) Time MW, 300 W 120 5–10 min (54) — 82 0.5–4 h (20)	22
		MeCN/DMF (10:1)	 Temp (°) Time MW, 300 W 120 5–10 min (62) — 82 0.5–4 h (62)	22
		MeCN/DMF (10:1)	 Temp (°) Time MW, 300 W 120 5–10 min (87) — 82 0.5–4 h (87)	22
		MeCN/DMF (10:1)	 Temp (°) Time MW, 300 W 120 5–10 min (15) — 82 0.5–4 h (<5)	22
		MeCN/DMF (10:1)	 Temp (°) Time MW, 300 W 120 5–10 min (95) — 82 0.5–4 h (95)	22

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

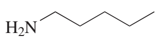
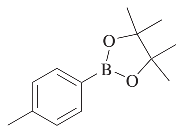
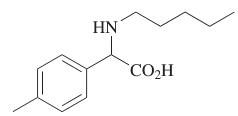
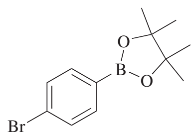
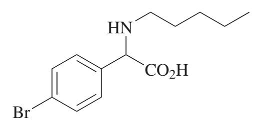
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

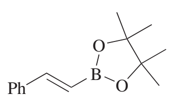
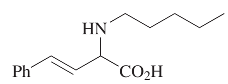
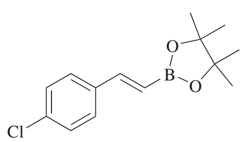
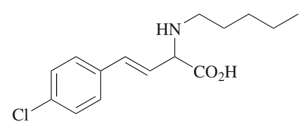
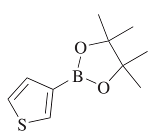
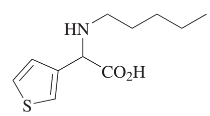
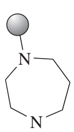
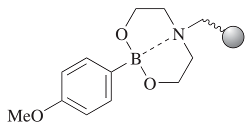
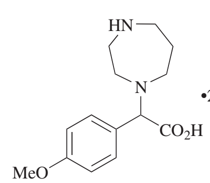
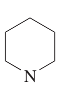
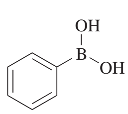
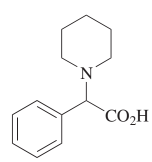
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		MeCN/DMF (10:1)		22

	Temp (°)	Time	
MW, 300 W	120	5–10 min	(65)
—	82	0.5–4 h	(65)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN/DMF (10:1)		22

	Temp (°)	Time	
MW, 300 W	120	5–10 min	(25)
—	82	0.5–4 h	(25)

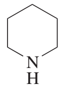
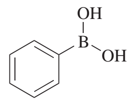
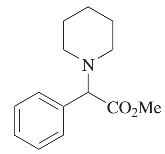
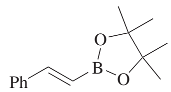
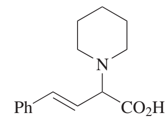
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt	 (0)	19
		CH_2Cl_2, rt	 (0)	19

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt	 (0)	19
		CH_2Cl_2, rt	 (0)	19
		CH_2Cl_2, rt	 (0)	19
		1. THF/EtOH (8:3), 65°, 24-48 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 •$2CF_3CO_2H$ (91)[d]	32, 91
		Solvent(s), rt, 20 h		18

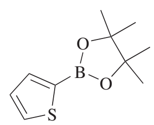
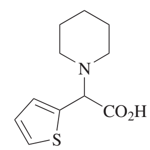
Solvent(s)		Conv (%)
CH_2Cl_2/HFIP (9:1)	(—)	68
CH_2Cl_2	(—)	15

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

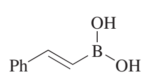
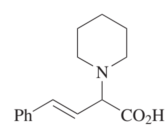
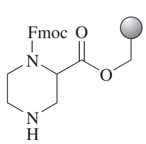
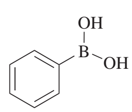
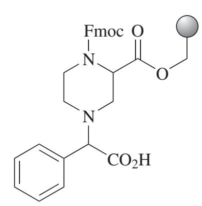
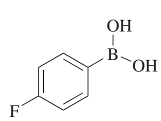
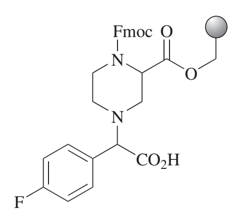
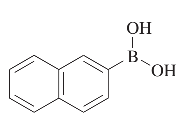
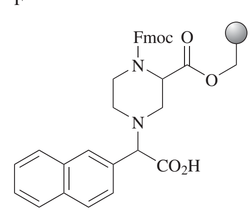
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		1. CH_2Cl_2/HFIP (9:1), rt, 45 h 2. $TMSCHN_2$	 (86)[b]	18
		See table.		21

Solvent		Temp	Time	
CH_2Cl_2	—	rt	—	(62)
CH_2Cl_2	MW	120°	10 min	(62)
MeOH	—	rt	72 h	(92)
MeOH	MW	120°	10 min	(89)
HFIP	—	rt	4 h	(90)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		See table.		21

	Solvent	Temp	Time	
MW, 300W	MeOH	120°	10 min	(88)
—	HFIP	rt	4 h	(85)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		H_2O, 50°, 24 h	 (67)	56
		CH_2Cl_2, rt	 (94) 85% pure [h]	94
		CH_2Cl_2, rt	 (93) 88% pure [h]	94
		CH_2Cl_2, rt	 (70.5) 76% pure [h]	94

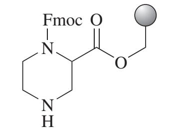
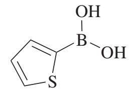
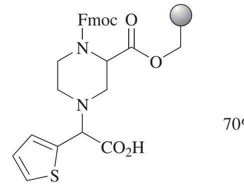
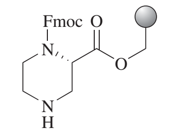
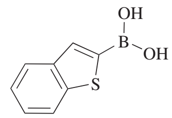
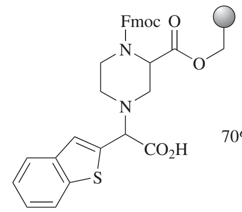
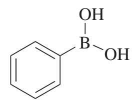
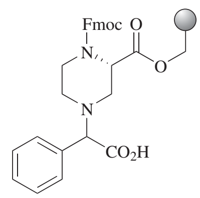
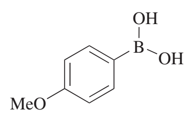
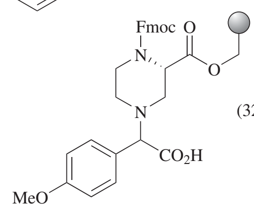
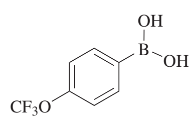
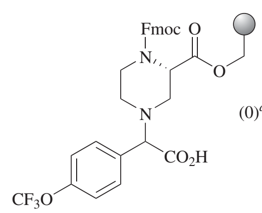
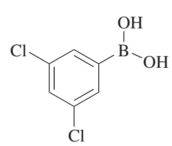
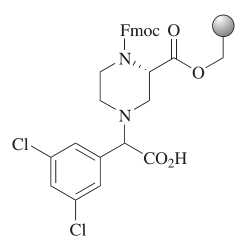
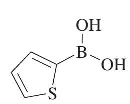
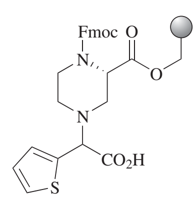
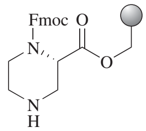
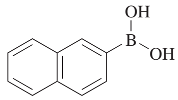
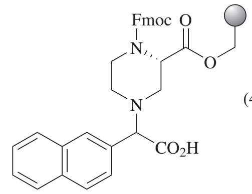
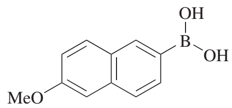
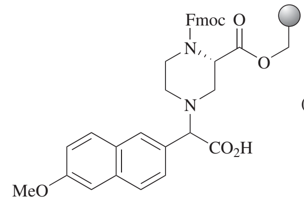
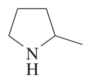
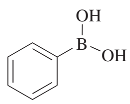
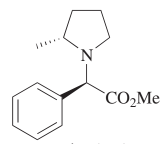
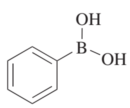
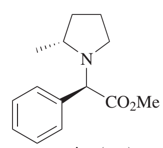
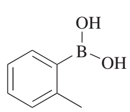
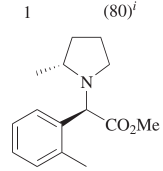
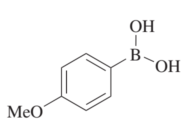
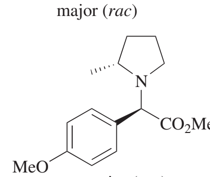
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_5 		CH_2Cl_2, rt	 (81) 70% pure [h]	94
		CH_2Cl_2, rt	 (96) 70% pure [h]	94
		CH_2Cl_2/MeOH (4:1), rt	 (47)[a]	95
		CH_2Cl_2/MeOH (4:1), rt	 (32)[a]	95
		CH_2Cl_2/MeOH (4:1), rt	 (0)[a]	95
		CH_2Cl_2/MeOH (4:1), rt	 (0)[a]	95
		CH_2Cl_2/MeOH (4:1), rt	 (18)[a]	95

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		CH_2Cl_2/MeOH (4:1), rt	 (45)[a]	95
		CH_2Cl_2/MeOH (4:1), rt	 (31)[a]	95
		1. MeCN, reflux, 7 h 2. $TMSCHN_2$	 major (*rac*) (65) dr 83:17	18
		1. Solvent(s), rt 2. $TMSCHN_2$	 major (*rac*)	18

Solvent(s)	Time (days)		dr
MeCN	8	(64)[i]	94:6
CH_2Cl_2	6	(80)[i]	>95:5
toluene	6	(53)[i]	93:7
EtOH	6	(53)[i]	93:7
CF_3CH_2OH	6	(78)[i]	>95:5
$(CF_3)_2CHOH$	6	(26)[j]	—
CH_2Cl_2/HFIP (9:1)	1	(80)[i]	>95:5

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. CH_2Cl_2/HFIP (9:1), rt, 24 h 2. $TMSCHN_2$	 major (*rac*) (91)[k] dr >95:5	18
		1. CH_2Cl_2/HFIP (9:1), rt, 20 h 2. $TMSCHN_2$	 major (*rac*) (93)[k] dr 94:6	18

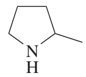
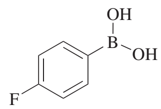
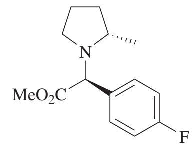
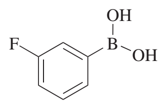
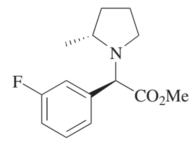
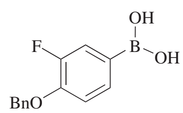
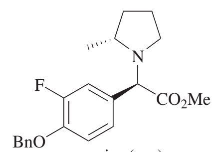
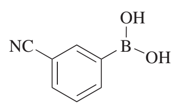
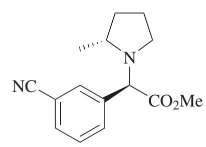
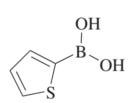
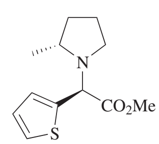
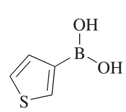
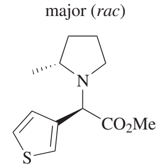
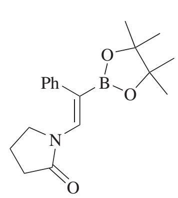
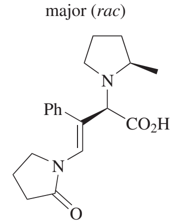
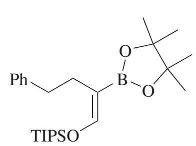
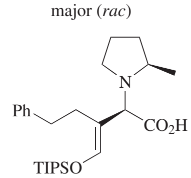
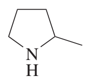
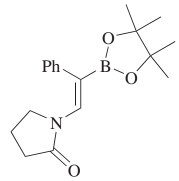
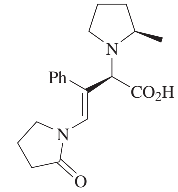
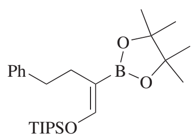
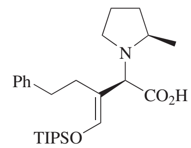
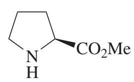
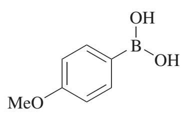
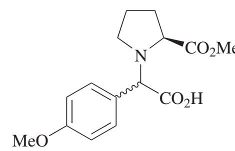
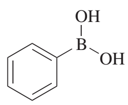
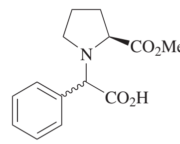
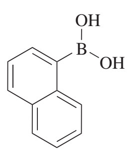
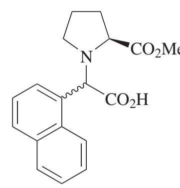
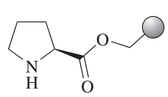
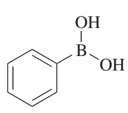
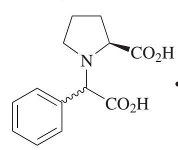
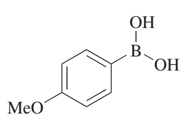
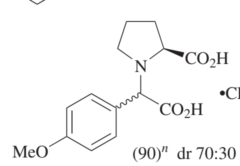
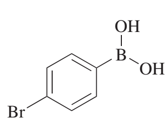
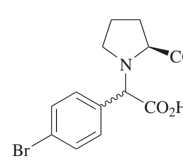
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_5				
		1. CH_2Cl_2/HFIP (9:1), rt, 24 h 2. $TMSCHN_2$	 major (*rac*) (83)[i] dr 95:5	18
		1. CH_2Cl_2/HFIP (9:1), rt, 22 h 2. $TMSCHN_2$	 major (*rac*) (71)[i] dr 95:5	18
		1. CH_2Cl_2/HFIP (9:1), rt, 17 h 2. $TMSCHN_2$	 major (*rac*) (88)[l] dr 87:13	18
		1. CH_2Cl_2/HFIP (9:1), rt, 22 h 2. $TMSCHN_2$	 major (*rac*) (0) dr —	18
		1. CH_2Cl_2/HFIP (9:1), rt, 7 h 2. $TMSCHN_2$	 major (*rac*) (59)[m] dr 57:43	18
		1. CH_2Cl_2/HFIP (9:1), rt, 7 h 2. $TMSCHN_2$	 major (*rac*) (70)[l] dr 91:9	18
		HFIP, 50°, 72 h	 major (*rac*) (85) dr >95:5	90
		HFIP, rt, 5 h	 major (*rac*) (67) dr >95:5	90

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_5				
		HFIP, 50°, 72 h	 major (*rac*) (85) dr >95:5	90
		HFIP, rt, 5 h	 major (*rac*) (67) dr >95:5	90
		CH_2Cl_2, rt	 Time (h) 48: (32)[a] dr 70:30	25
			Time (h) 24: (34)[a] dr 50:50	96
		CH_2Cl_2, rt, 24 h	 (32)[a] dr 50:50	96
		CH_2Cl_2, rt, 24 h	 (48)[a] dr 50:50	96
		1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •CF_3CO_2H (82)[n] dr 88:12 >95% pure	13
		1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •CF_3CO_2H (90)[n] dr 70:30 >95% pure	13
		1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •CF_3CO_2H (86)[n] dr 73:27 92% pure	13

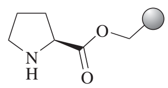
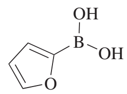
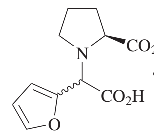
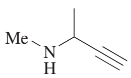
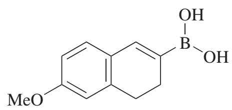
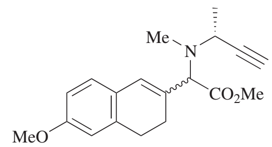
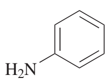
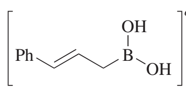
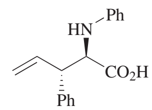
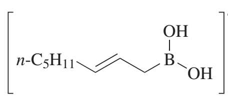
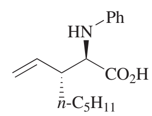
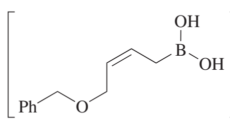
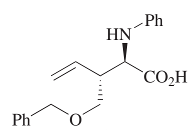
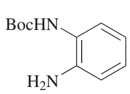
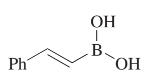
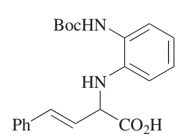
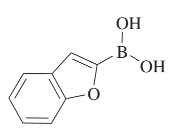
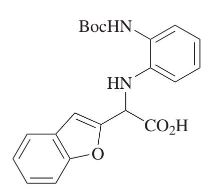
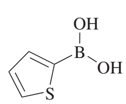
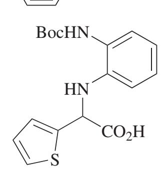
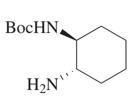
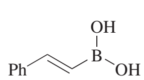
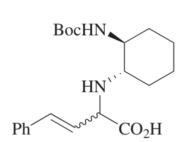
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_5				
		1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •CF_3CO_2H (78)[n] dr 54:46 90% pure	13
		1. CH_2Cl_2, rt, 12 h 2. CH_2N_2, Et_2O	 (92) dr 50:50 (*rac*)	97
C_6				
	[o]	DMSO/MeOH, rt, 16 h	 (78)[o] major (*rac*)	30
	[o]	DMSO/MeOH, rt, 16 h	 (77)[o] major (*rac*)	30
	[o]	DMSO/MeOH, rt, 16 h	 (77)[o] major (*rac*)	30
		MeCN, 80°, 6 h	 (88)	62
		MeCN, 80°, 2 h	 (63)[a]	62
		MeCN, 80°, 2 h	 (70)[a]	62
		CH_2Cl_2, rt	 (73) dr 86.5:13.5	62

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

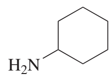
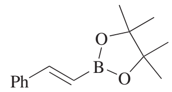
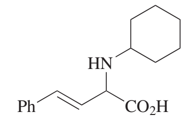
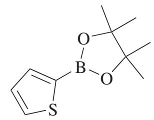
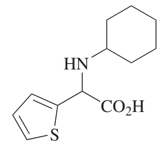
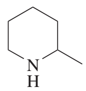
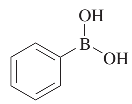
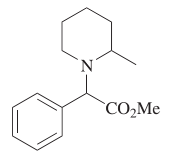
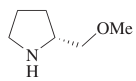
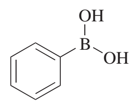
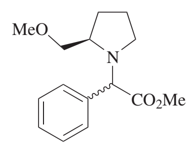
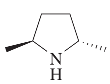
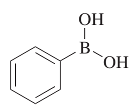
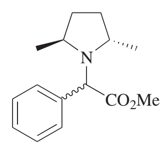
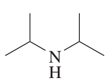
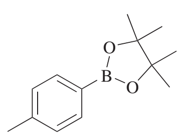
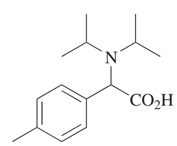
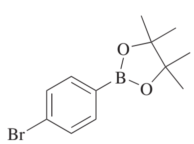
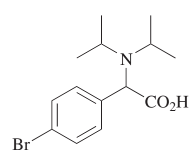
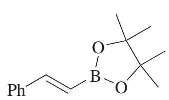
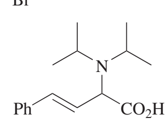
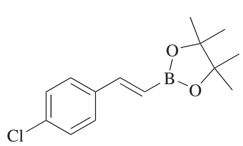
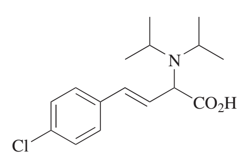
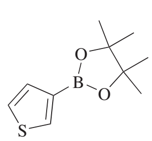
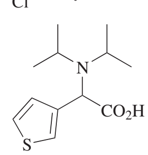
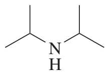
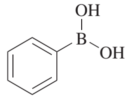
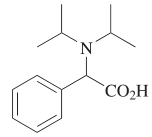
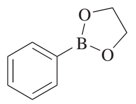
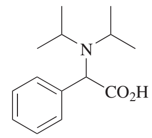
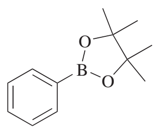
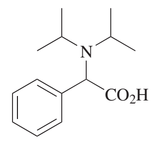
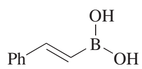
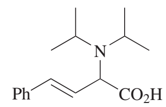
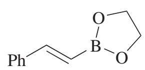
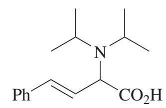
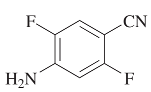
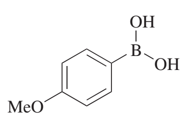
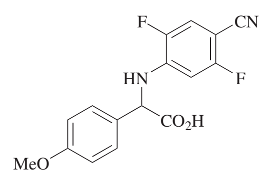
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_6				
		Solvent, rt	 Solvent / Time (h): MeOH 72 (60); HFIP 4 (78)	21
		Solvent, rt	 Solvent / Time (h): MeOH 72 (35); HFIP 4 (75)	21
		1. CH_2Cl_2/HFIP (9:1), rt, 24 h 2. $TMSCHN_2$	 (0) dr —	18
		1. CH_2Cl_2/HFIP (9:1), rt, 24 h 2. $TMSCHN_2$	 (85)[i] dr >95:5	18
		1. CH_2Cl_2/HFIP (9:1), rt, 24 h 2. $TMSCHN_2$	 (0)	18
		CH_2Cl_2, rt	 (12)	19
		CH_2Cl_2, rt	 (6)	19
		CH_2Cl_2, rt	 Time: — (75)[f] 48 h (0)	19 31
		CH_2Cl_2, rt	 (70)[f]	19
		CH_2Cl_2, rt	 (27)	19

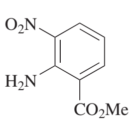
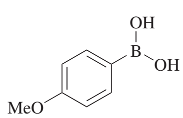
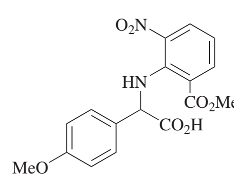
TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

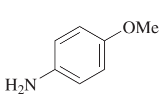
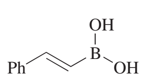
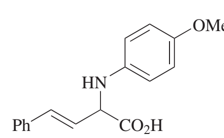
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		CH_2Cl_2, rt, 48 h	 (84)	31
		CH_2Cl_2, rt, 48 h	 (19)	31
		CH_2Cl_2, rt, 48 h	 (0)	31
		CH_2Cl_2, rt, 48 h	 (84)	31
		CH_2Cl_2, rt, 48 h	 (19)	31

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		MeCN/DMF (10:1)		22

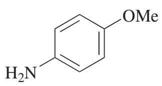
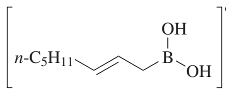
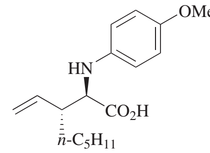
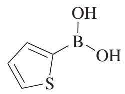
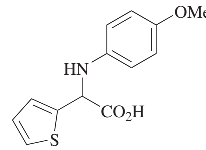
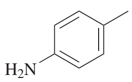
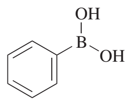
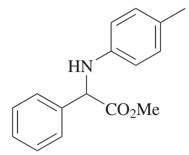
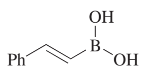
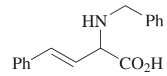
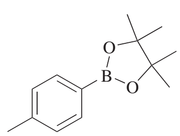
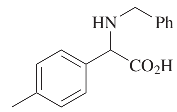
	Temp (°)	Time	
MW, 300 W	120	5–10 min	(79)
—	82	0.5–4 h	(79)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN/DMF (10:1)		22

	Temp (°)	Time	
MW, 300 W	120	5–10 min	(0)
—	82	0.5–4 h	(0)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		EtOH, rt, 12–48 h	 (94)	33

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	 [o]	DMSO/MeOH, rt, 8 h	 major (*rac*) (52)[o]	30
		EtOH, rt, 12 h	 (79)	86
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, 3 h	 (27)	50
		EtOH, rt, 12–48 h	 (87)	33
		See table.		19

	Solvent	Catalyst	Temp	
—	CH_2Cl_2	—	rt	(0)
—	CH_2Cl_2	$Yb(OTf)_3$	rt	(0)
—	THF	—	reflux	(0)
—	dioxane	—	reflux	(0)
—	toluene	—	reflux	(0)
MW	DMF	—	250°	(0)

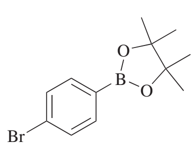
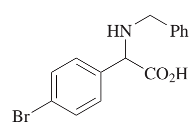
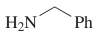
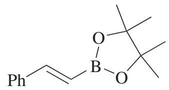
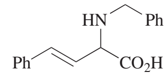
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt	 (0)	19

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Solvent(s), rt		

Solvent(s)	Time (h)		Conv (%)	Refs.
CH_2Cl_2	—	(0)	—	19
CH_2Cl_2	48	(0)	—	31
toluene	4	(—)	0	21
THF	4	(—)	0	21
CH_2Cl_2	4	(—)	0	21
dioxane	4	(—)	0	21
MeOH	4	(—)	52	21
CF_3CH_2OH	4	(—)	74	21
$(CF_3)_2CHOH$	4	(—)	88	21
CH_2Cl_2/MeOH (9:1)	4	(—)	24	21
CH_2Cl_2/TFE (9:1)	4	(—)	34	21
CH_2Cl_2/HFIP (9:1)	4	(—)	42	21
MeOH/HFIP (9:1)	4	(—)	53	21
MeOH	24	(60)	65	21
MeOH	72	(67)	100	21
HFIP	4	(85)	—	21

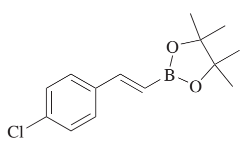
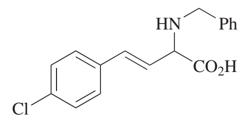
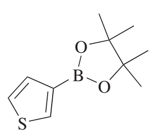
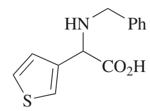
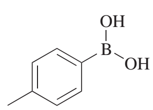
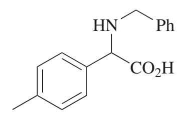
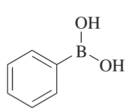
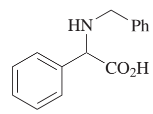
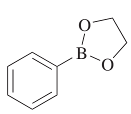
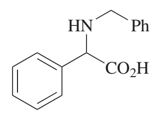
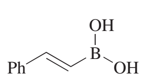
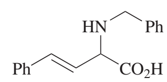
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt	 (0)	19
		CH_2Cl_2, rt	 (0)	19
		CH_2Cl_2, rt	 (67)	19
		CH_2Cl_2, rt, 48 h	 (10)	31
		CH_2Cl_2, rt, 48 h	 (0)	31
		CH_2Cl_2, rt, 48 h	 (79)	31

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

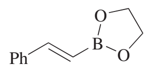
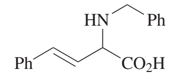
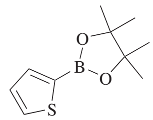
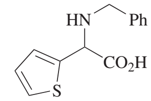
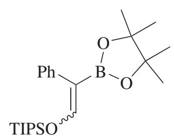
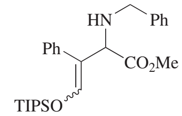
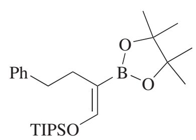
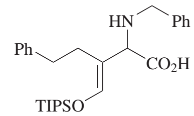
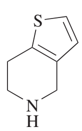
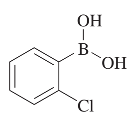
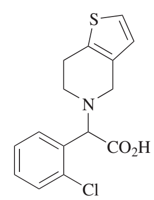
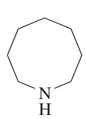
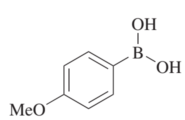
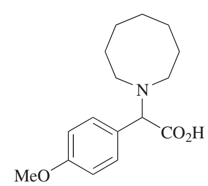
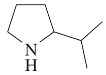
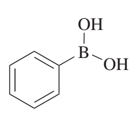
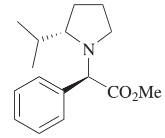
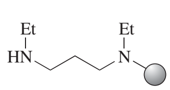
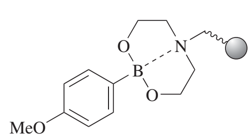
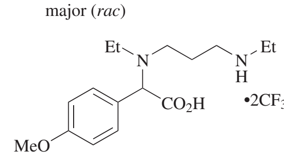
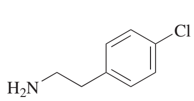
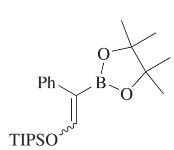
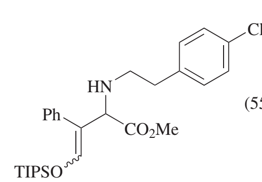
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		CH_2Cl_2, rt, 48 h	 (20)	31
		Solvent, rt	 Solvent / Time (h): MeOH 72 (40); HFIP 4 (90)	21
	 (*E*)/(*Z*) = 40:60	1. HFIP, rt, 48 h 2. $TMSCHN_2$, $MeOH/CH_2Cl_2$ (1:2), rt, 1 h	 (50) (*E*)/(*Z*) = 80:20	90
		HFIP, rt, 5 h	 (67)	90
		DMF, rt, 7 d	 (49)	98
		CH_2Cl_2, rt, 48 h	 (73)[a]	25, 26
		1. CH_2Cl_2/HFIP (9:1), rt, 19 h 2. $TMSCHN_2$	 major (*rac*) (90)[i] dr >95:5	18
		1. THF/EtOH (8:3), 65°, 24–48 h 2. TFA/CH_2Cl_2 (1:20), rt, 1 h	 •$2CF_3CO_2H$ (82)[d]	32, 91
C_8				
	 (*E*)/(*Z*) = 40:60	1. HFIP, rt, 48 h 2. $TMSCHN_2$, $MeOH/CH_2Cl_2$ (1:2), rt, 1 h	 (55) (*E*)/(*Z*) = 75:25	90

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

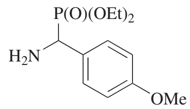
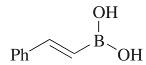
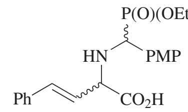
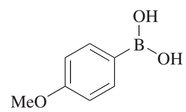
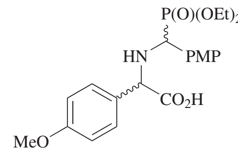
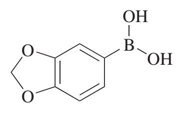
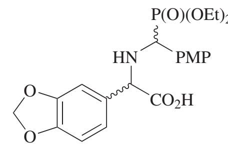
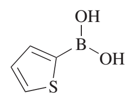
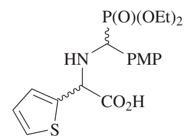
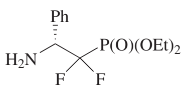
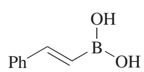
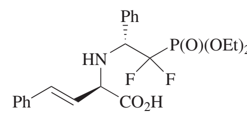
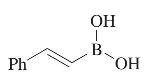
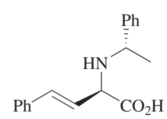
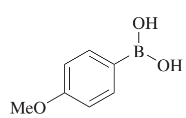
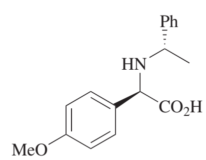
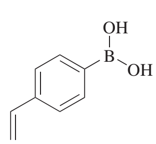
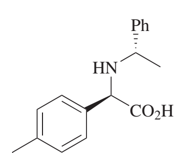
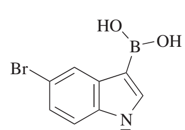
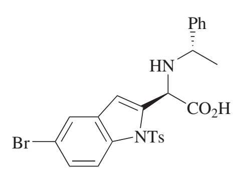
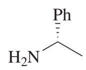
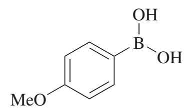
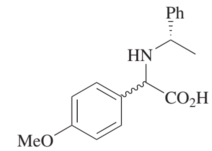
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		EtOAc, reflux, 2.5 h	 (75)[i] Time (h) 2.5, dr 90:10	92
			Time (h) 2–2.5, dr >9:1	93
		EtOAc, reflux, 2.5 h	 (76)[i] dr 90:10	92
		EtOAc, reflux, 4 h	 (53) dr 90:10	92
		EtOAc, reflux, 4 h	 (43) dr 90:10	92
		CH_2Cl_2, rt, 24 h	 major (55) dr 60:40	92
		CH_2Cl_2, rt	 major; Time (h) 12: (88) dr 83:17	33
			Time (h) 48: (81) dr 3.3:1	31
		Toluene, rt	 major (82) dr 67.5:32.5	86
		Toluene, rt	 major (77) dr 64:36	86
		CH_2Cl_2, rt, 24 h	 major (64) dr 99.5:0.5	99

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

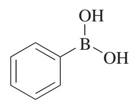
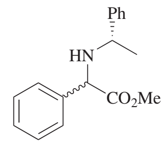
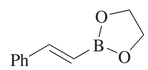
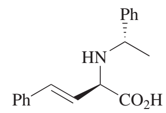
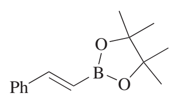
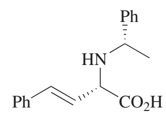
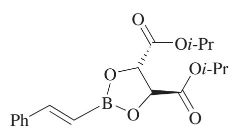
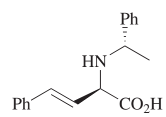
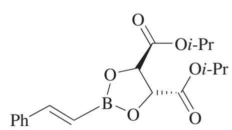
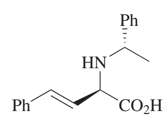
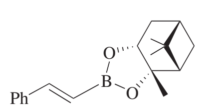
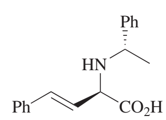
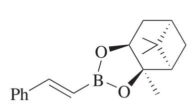
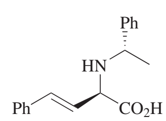
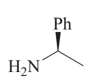
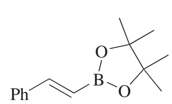
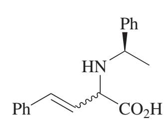
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

C_8

		See table.		18

Solvent(s)	Temp	Time (h)	Conv (%) [p]		dr
toluene	rt	1	46	(—)	—
CH_2Cl_2/HFIP (9:1)	rt	1	96	(—)	—
toluene	0°	5.5	36	(—)	—
CH_2Cl_2/HFIP (9:1)	0°	5.5	94	(92)	69:31

		1. CH_2Cl_2/HFIP (9:1), rt, 24 h 2. $TMSCHN_2$	 (0)[b] dr —	18
		CH_2Cl_2, rt, 48 h	 major (47) dr 3.2:1	31
		CH_2Cl_2, rt, 48 h	 major (7) dr 1:1.4	31
		CH_2Cl_2, rt, 48 h	 major (75) dr 3.5:1	31
		CH_2Cl_2, rt, 48 h	 major (55) dr 2.5:1	31
		CH_2Cl_2, rt, 48 h	 (0)	31
		CH_2Cl_2, rt, 48 h	 (0)	31
		Solvent, rt		21

Solvent	Time (h)		dr
MeOH	72	(70)	66.5:33.5
HFIP	4	(77)	90.5:9.5

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

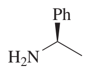
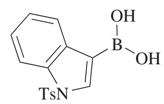
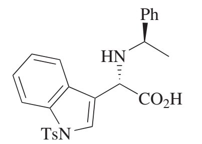
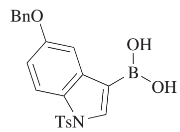
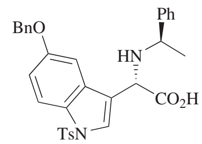
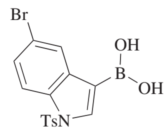
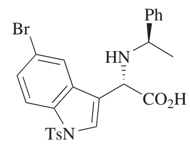
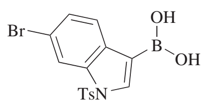
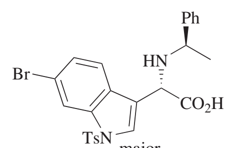
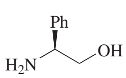
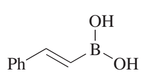
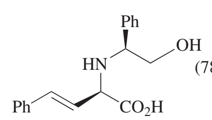
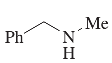
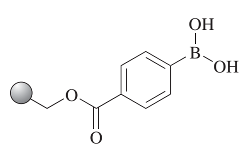
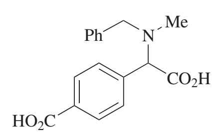
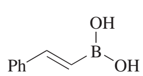
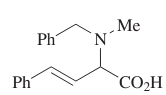
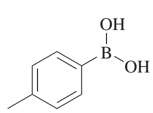
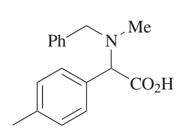
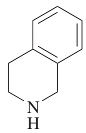
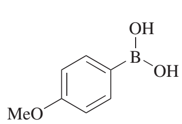
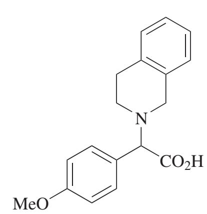
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_8				
		CH_2Cl_2, rt, 24 h	 major (77) dr 99.5:0.5	99
		CH_2Cl_2, rt, 24 h	 major (68) dr 99.5:0.5	99
		CH_2Cl_2, rt, 24 h	 major (64) dr 99.5:0.5	99
		CH_2Cl_2, rt, 24 h	 major (71) dr 99.5:0.5	99
		CH_2Cl_2, rt, 12 h	 major (78) dr 99.5:0.5	33
		1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 •CF_3CO_2H (14)[c] 73% pure	13
		H_2O, 50°, 36 h	 (77)	56
		H_2O, 80°, 36 h	 (65)	56
C_9				
		CH_2Cl_2, rt, 48 h	 (54)[a]	25, 26

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

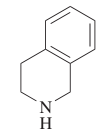
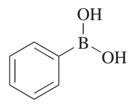
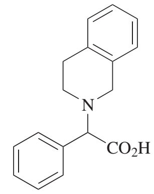
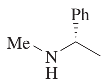
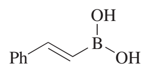
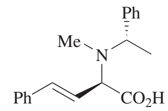
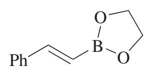
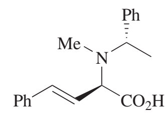
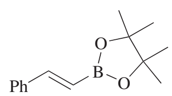
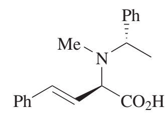
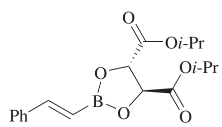
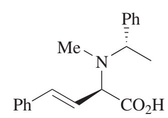
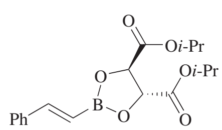
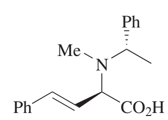
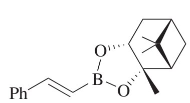
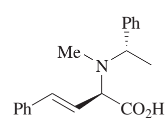
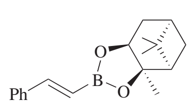
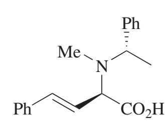
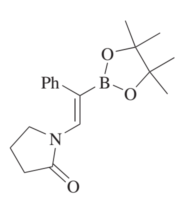
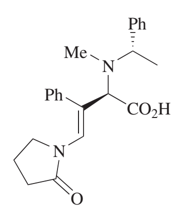
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)		Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.					
C_9					
		CH_2Cl_2, rt, 48 h		(50)[a]	26
		CH_2Cl_2, rt, 48 h	 major	(89) dr >95:5	31
		CH_2Cl_2, rt, 48 h	 major	(49) dr >95:5	31
		CH_2Cl_2, rt, 48 h	 major	(21) dr >95:5	31
		CH_2Cl_2, rt, 48 h	 major	(60) dr >95:5	31
		CH_2Cl_2, rt, 48 h	 major	(50) dr >95:5	31
		CH_2Cl_2, rt, 48 h	 major	(7) dr >95:5	31
		CH_2Cl_2, rt, 48 h	 major	(1) dr >95:5	31
		HFIP, 50°, 72 h	 major	(51) dr 75:25	90

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

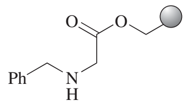
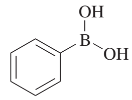
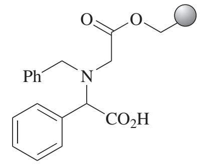
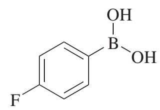
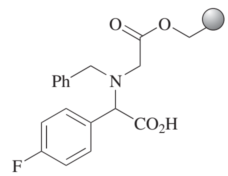
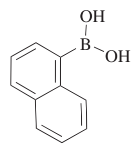
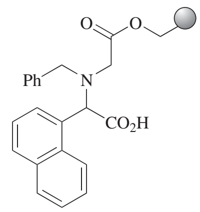
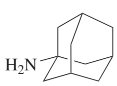
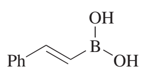
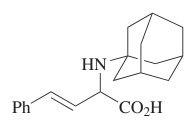
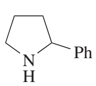
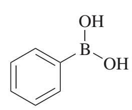
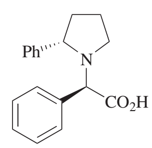
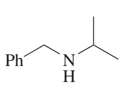
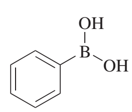
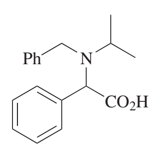
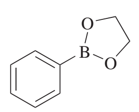
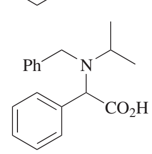
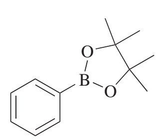
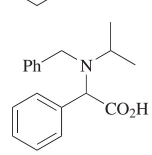
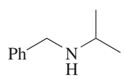
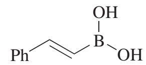
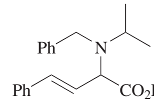
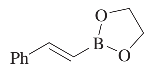
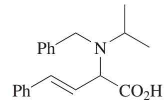
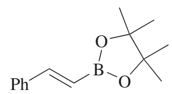
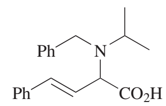
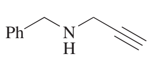
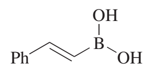
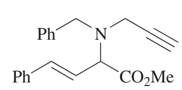
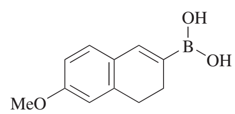
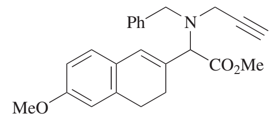
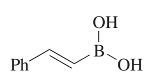
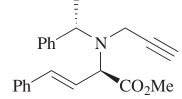
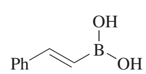
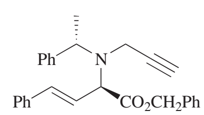
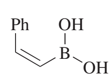
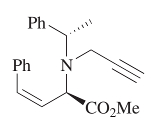
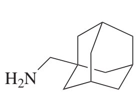
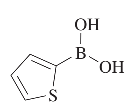
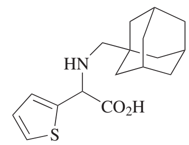
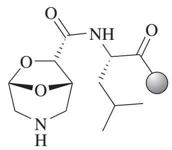
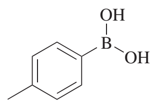
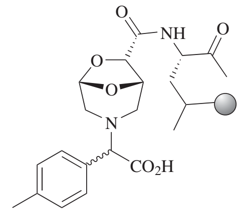
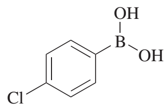
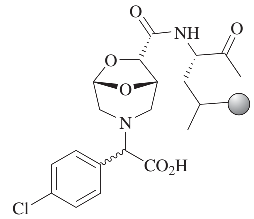
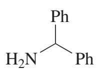
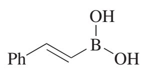
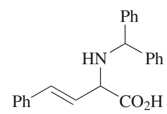
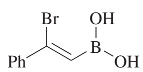
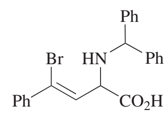
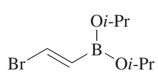
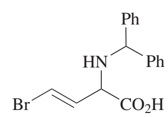
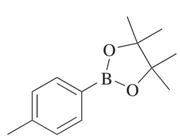
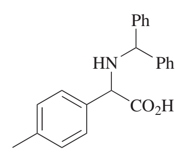
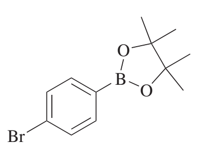
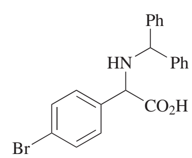
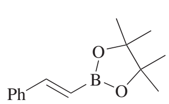
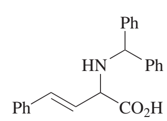
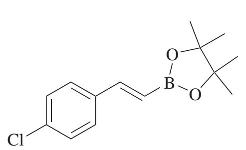
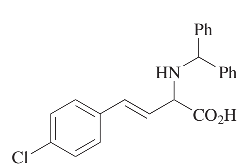
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_9				
		CH_2Cl_2, rt, 78 h	 (91) 88% pure[q]	100
		CH_2Cl_2, rt, 78 h	 (84) 57% pure[q] (66) 77% pure[q]	100
		CH_2Cl_2, rt, 78 h	 (67) 75% pure[q]	100
C_{10}				
		See table.		
		Solvent / Temp / Time (h)		
		CH_2Cl_2 / rt / 12–48	(96)	33
		H_2O / 80° / 24	(72)	56
		CH_2Cl_2/HFIP (9:1), rt, 24 h	 major (*rac*) (96)[i] dr >95:5	18
		CH_2Cl_2, rt, 48 h	 (89)	31
		CH_2Cl_2, rt, 48 h	 (43)	31
		CH_2Cl_2, rt, 48 h	 (0)	31

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_{10}				
		CH_2Cl_2, rt, 48 h	 (90)	31
		CH_2Cl_2, rt, 48 h	 (39)	31
		CH_2Cl_2, rt, 48 h	 (5)	31
		1. CH_2Cl_2, rt, 12 h 2. CH_2N_2	 (95)	36
		1. CH_2Cl_2, rt, 12 h 2. CH_2N_2, Et_2O	 (92)	97
		1. Et_3N (*x* eq), CH_2Cl_2, rt, 12 h 2. CH_2N_2	 major *x* / Time (h) / dr 0 / 12 / (90) 1.5:1 2 / 24 / (90) 7.5:2.5	36
		1. Et_3N (*x* eq), CH_2Cl_2, rt, 12 h 2. $PhCH_2OH$	 major *x* / Time (h) / dr 0 / 12 / (87) 1.5:1 2 / 24 / (88) 7.5:2.5	36
		1. Et_3N (*x* eq), CH_2Cl_2, rt, 12 h 2. CH_2N_2	 major *x* / Time (h) / dr 0 / 12 / (92) 1.5:1 2 / 24 / (92) 7.5:2.5	36
		CH_2Cl_2, rt, 12 h	 (90)	86

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_{12}				
		$CHCl_3$/EtOH (3:1), 50°, 12 h	 (30) dr 92:8^{r}	101
		$CHCl_3$/EtOH (3:1), 50°, 12 h	 (16), 60:40^{r}	101
C_{13}				
		Toluene, rt, 12–48 h	 (94)	33
		Toluene, rt, 12–48 h	 (87)	33
		CH_2Cl_2, rt, 12–48 h	 (80)	33
		CH_2Cl_2, rt	 (0)	19
		CH_2Cl_2, rt	 (0)	19
		Solvent, rt	 Solvent: CH_2Cl_2, Time: —, (0)	19
			Solvent: MeOH, Time: 72 h, (64)	21
			Solvent: HFIP, Time: 4 h, (92)	21
		CH_2Cl_2, rt	 (0)	19

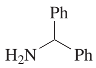
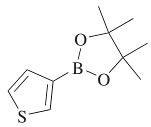
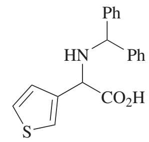
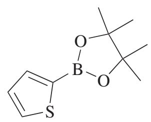
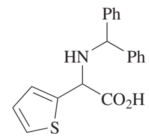
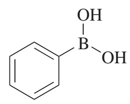
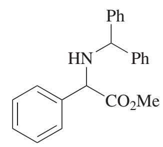
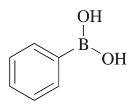
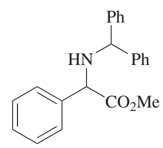
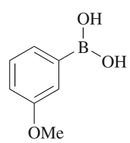
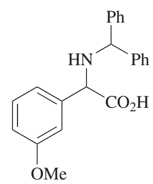
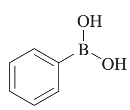
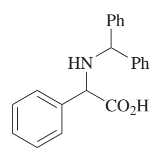
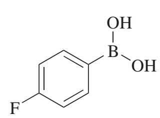
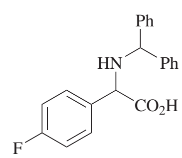
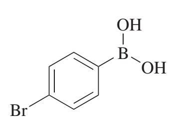
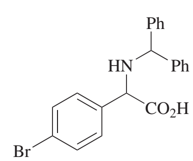
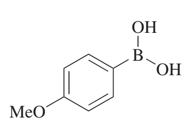
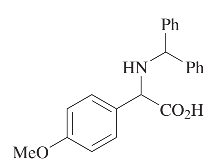
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_{13} 		CH_2Cl_2, rt	 (0)	19
		Solvent, rt	 Solvent / Time (h) MeOH / 72 / (78) HFIP / 4 / (79)	21
		1. CH_2Cl_2/HFIP (9:1), rt, 30 h 2. $TMSCHN_2$	 (54)[b]	18
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, 3 h	 (17), 50% conv	50
		Toluene, rt, 48 h	 (29)	86
		Toluene, rt, 48 h	 (84)	86
		Toluene, rt, 48 h	 (50)	86
		Toluene, rt, 48 h	 (71)	86
		Toluene, rt, 48 h	 (85)	86

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

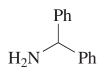
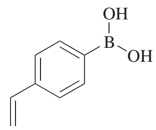
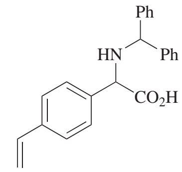
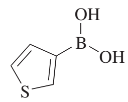
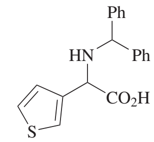
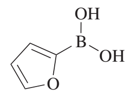
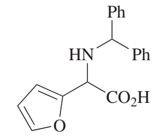
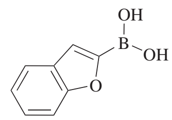
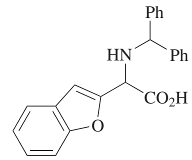
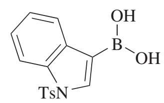
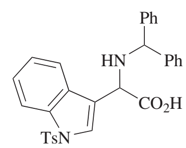
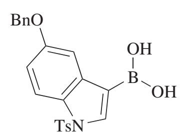
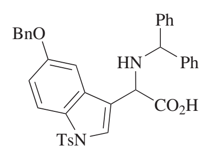
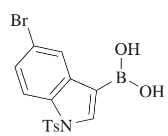
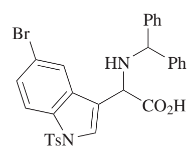
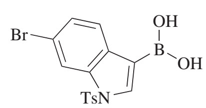
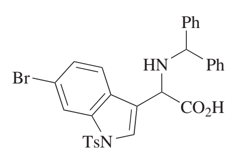
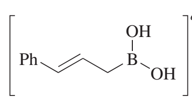
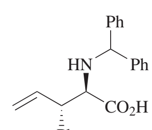
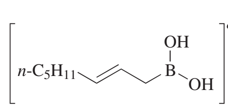
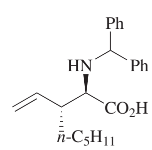
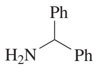
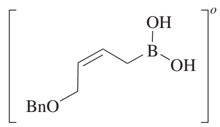
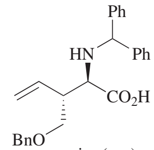
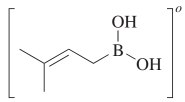
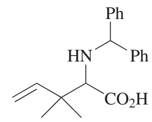
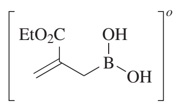
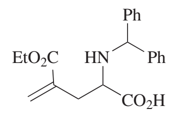
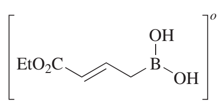
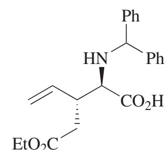
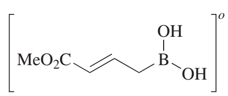
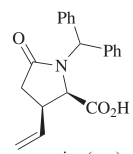
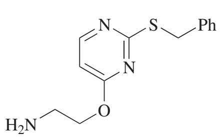
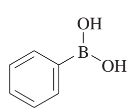
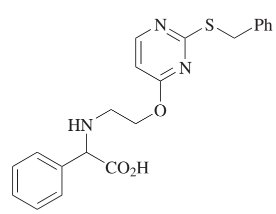
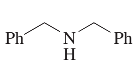
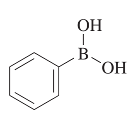
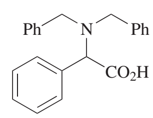
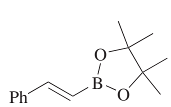
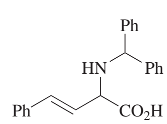
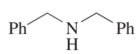
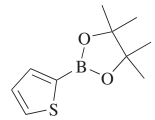
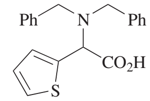
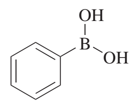
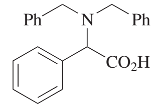
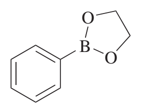
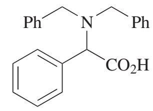
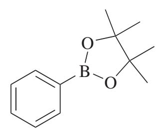
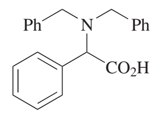
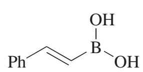
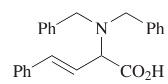
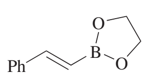
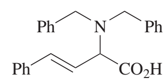
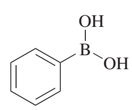
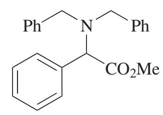
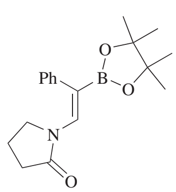
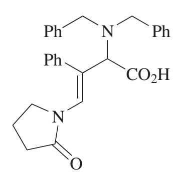
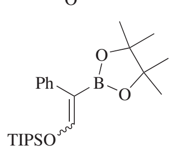
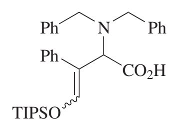
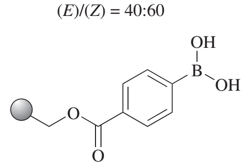
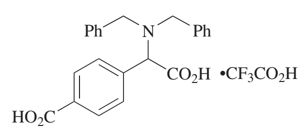
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)		Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.					
C_{13}					
		Toluene, rt, 48 h		(90)	86
		CH_2Cl_2, rt, 8 h		(92)	86
		CH_2Cl_2, rt, 4 h		(81)	86
		CH_2Cl_2, rt, 4 h		(84)	86
		CH_2Cl_2, rt, 12 h		(94)	99
		CH_2Cl_2, rt, 12 h		(91)	99
		CH_2Cl_2, rt,12 h		(93)	99
		CH_2Cl_2, rt, 12 h		(90)	99
	 [o]	DMSO/MeOH, rt, 16 h	 major (*rac*)	(76)[o]	30
	 [o]	DMSO/MeOH, rt, 16 h	 major (*rac*)	(83)[o]	30

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_{13}				
		DMSO/MeOH, rt, 16 h	 major (*rac*) (75)[o]	30
		DMSO/MeOH, rt, 24 h	 (60)[o]	30
		DMSO/MeOH, rt, 16 h	 (68)[o]	30
		DMSO/MeOH, rt, 16 h	 major (*rac*) (78)[o]	30
		DMSO/MeOH, rt, 16 h	 major (*rac*) (80)[o]	30
		CH_2Cl_2, rt	 (0)	102
C_{14}				
		H_2O, 50°, 24 h	 (86)	56
		See table.		

	Solvent	Temp	Time		Refs.
MW, 300 W	MeOH	120°	10 min	(67)	21
—	HFIP	rt	4 h	(97)	21
—	CH_2Cl_2	rt	48 h	(90)	31

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_{14}				
		See table.		21
		CH_2Cl_2, rt, 48 h	 (64)	31
		CH_2Cl_2, rt, 48 h	 (35)	31
		CH_2Cl_2, rt, 48 h	 (35)	31
		CH_2Cl_2, rt, 48 h	 (64)	31
		CH_2Cl_2, rt, 48 h	 (77)	31
		1. CH_2Cl_2, MW, 120°, 10 min 2. $TMSCHN_2$, THF, 3 h	 (83)	50
		HFIP, 50°, 24 h	 (70)	90
	 (*E*)/(*Z*) = 40:60	HFIP, rt, 24 h	 (84) (*E*)/(*Z*) = 60:40	90
		1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 (20)[c] >95% pure	13

	Solvent	Temp	Time	
MW, 300 W	MeOH	120°	10 min	(78)
—	HFIP	rt	4 h	(85)

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

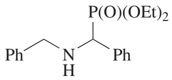
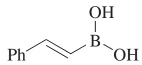
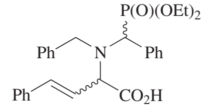
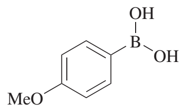
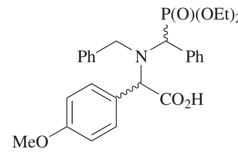
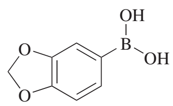
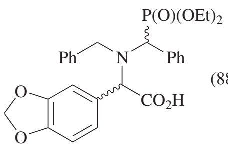
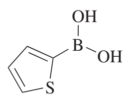
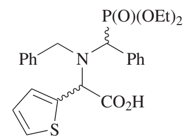
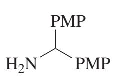
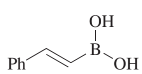
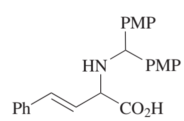
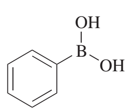
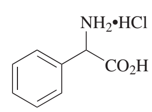
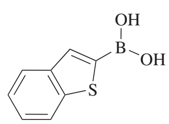
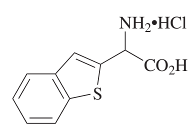
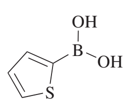
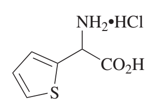
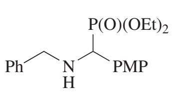
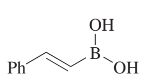
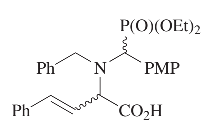
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_{14}				
		EtOAc, reflux, 2.5 h	 (80)[i] dr >95:5	92
		EtOAc, reflux	 (95)[i]	
			Time (h) 2.5, dr >95:5	92
			Time (h) 2–2.5, dr >9:1	93
		EtOAc, reflux	 (88)[i] Time (h) 2.5, dr >95:5	92
			Time (h) 2–2.5, dr >9:1	93
		EtOAc, reflux	 (69)[i] Time (h) 4, dr >95:5	92
			Time (h) 2–2.5, dr >9:1	93
C_{15}				
		Toluene, rt, 12–48 h	 (92)	33
		1. CH_2Cl_2 or toluene, rt, 48 h 2. AcOH, H_2O; then HCl, H_2O	 (62)	86
		1. CH_2Cl_2, rt, 12 h 2. AcOH, H_2O; then HCl, H_2O	 (80)	86
		1. CH_2Cl_2, rt, 12 h 2. AcOH, H_2O; then HCl, H_2O	 (79)	86
		EtOAc, reflux, 2–2.5 h	 (75) dr >9:1	93

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

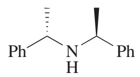
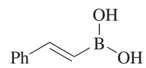
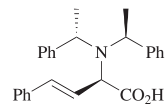
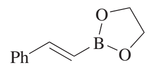
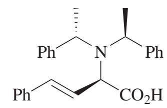
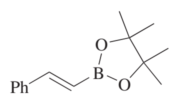
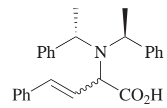
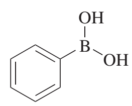
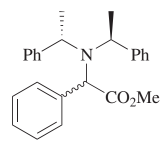
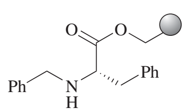
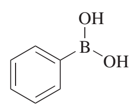
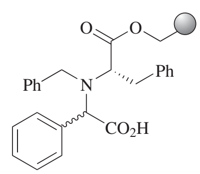
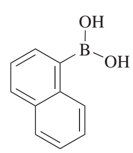
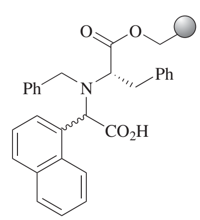
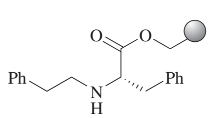
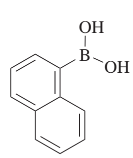
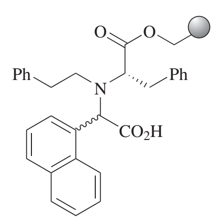
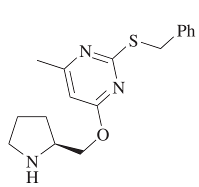
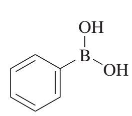
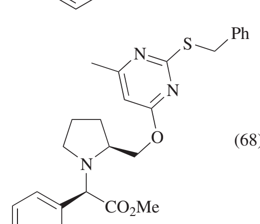
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.				
C_{16}				
		CH_2Cl_2, rt, 48 h	 major (38) dr >95:5	31
		CH_2Cl_2, rt, 48 h	 major (13) dr >95:5	31
		CH_2Cl_2, rt, 48 h	 (—)	31
		1. CH_2Cl_2/HFIP (9:1), rt, 24 h 2. $TMSCHN_2$,	 (0)[b]	18
		CH_2Cl_2, rt, 78 h	 (45) 76% pure[q]	100
		CH_2Cl_2, rt, 78 h	 (55) 86% pure[q]	100
C_{17}				
		CH_2Cl_2, rt, 78 h	 (42) 75% pure[q]	100
		1. CH_2Cl_2, rt 2. MeI, Cs_2CO_3, DMF, rt, 1 h	 major (68) dr 85:15	102

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

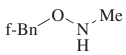
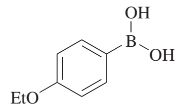
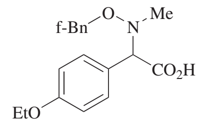
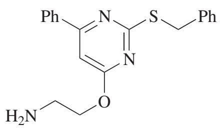
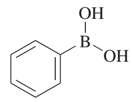
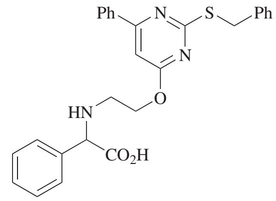
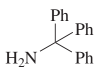
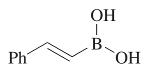
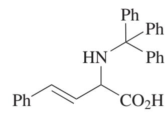
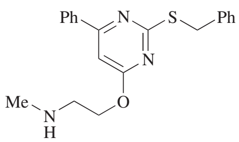
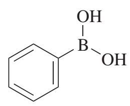
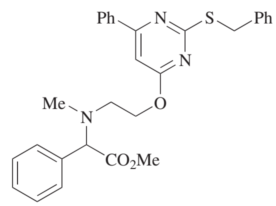
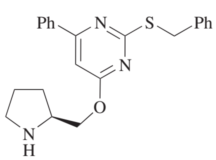
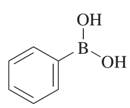
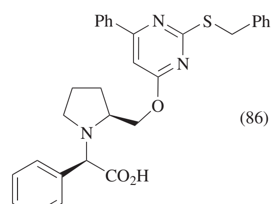
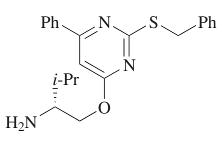
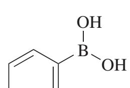
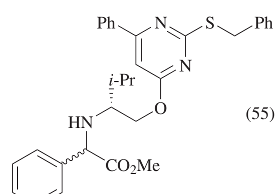
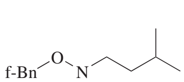
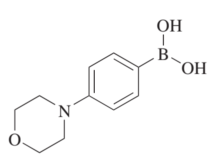
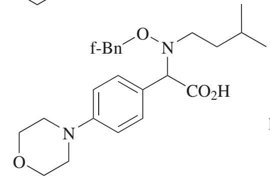
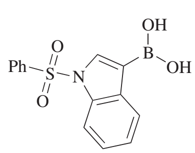
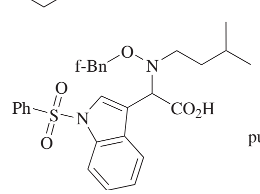
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}				
		CH_2Cl_2, rt, 20 h; [s] F-SPE	 (97) purity 100/92 [t]	103
C_{19}				
		CH_2Cl_2, rt	 (0)	102
		EtOH, rt, 12–48 h	 (54)	33
C_{20}				
		1. CH_2Cl_2, rt 2. MeI, Cs_2CO_3, DMF, rt, 1 h	 (50)	102
C_{22}				
		CH_2Cl_2, rt	 major (86) dr 86.5:13.5	102
		1. CH_2Cl_2, rt 2. MeI, Cs_2CO_3, DMF, rt, 1 h	 (55) dr 70:30	102
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (91) purity 68/100 [t]	103
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (92) purity 84/100 [t]	103

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 1.

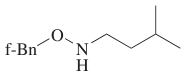
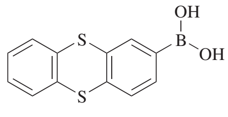
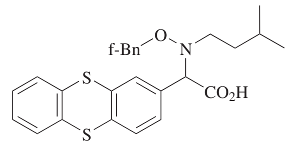
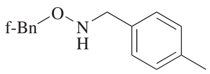
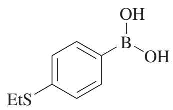
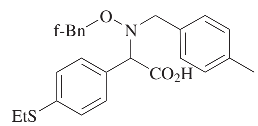
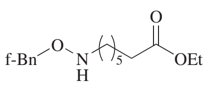
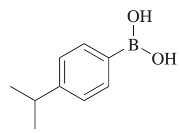
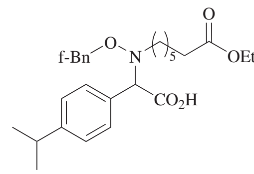
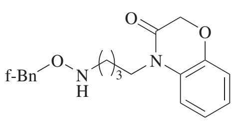
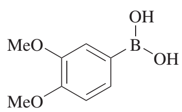
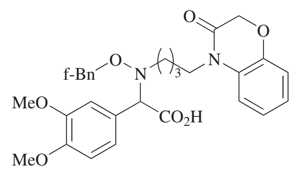
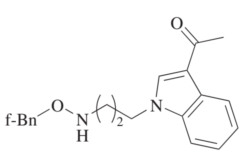
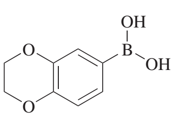
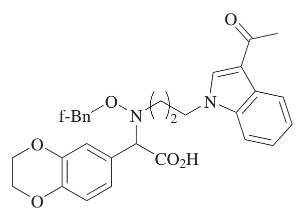
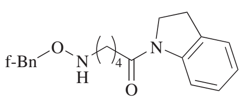
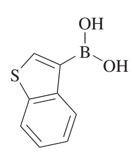
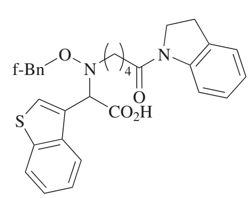
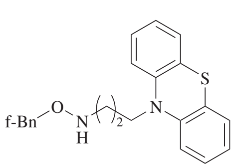
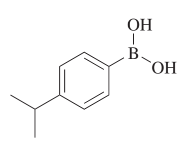
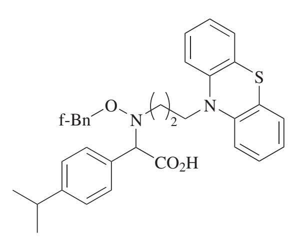
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22}				
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (99) purity 74/96 [t]	103
C_{25}				
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (94) purity 75/80 [t]	103
C_{26}				
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (96) purity 53/100 [t]	103
C_{29}				
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (43) purity 79/100 [t]	103
C_{30}				
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (84) purity 99/100 [t]	103
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (71) purity 97/100 [t]	103
C_{32}				
		CH_2Cl_2, rt, 48 h; [s] F-SPE	 (75) purity 89/100 [t]	103

TABLE 1. α-AMINO ACIDS FROM GLYOXYLIC ACID, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.

[a] The actual yield was not reported because this product was used in a multi-step synthesis. The overall yield of the final product was given.

[b] This value was reported as supporting information.

[c] The yield was determined by ^{1}H NMR using DMSO-d_5 as the internal standard, based on the theoretical loading of Wang aldehyde resin (2.45 mmol/g).

[d] The yields of crude products are based on ^{1}H NMR analysis with an internal standard.

[e] The yield was determined by ^{1}H NMR using DMSO-d_5 as the internal standard, based on the theoretical loading of Wang aldehyde resin (1.04 mmol/g).

[f] The yields were derived from HPLC analysis.

[g] The diasteromer ratio reported for the isolated material was 57:43.

[h] The actual yield was not reported because this product was used in a multi-step synthesis. The overall yield of the final crude product was given. The purity was determined by LC/MS with UV detection at 220 nm.

[i] These yields are of the major diastereomer.

[j] The percent conversion was estimated by LC/MS of the reaction mixture.

[k] The diasteromer ratio reported for the isolated material was >95:5.

[l] The diasteromer ratio reported for the isolated material was 86:14.

[m] The diasteromer ratio reported for the isolated material was 56:44.

[n] The yield was determined by ^{1}H NMR using DMSO-d_5 as the internal standard, based on the theoretical loading of the Fmoc-Proline Wang resin (0.84 mmol/g).

[o] The starting boronic acids were generated in situ from the corresponding alcohols. The reported yields are overall from the starting alcohols.

[p] See Ref. 13 in the original paper.

[q] The actual yield was not reported because this product was used in a multi-step synthesis. The overall yield of the final crude product was given. The purity was determined by LC–MS with ELSD.

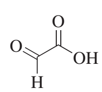
[r] The actual yield was not reported because this product was used in a multi-step synthesis. The overall yield of the final product was given based on resin loading as reported by the manufacturer. The diastereomer ratio was based on that of the final product.

[s] Glyoxylic acid was generated in situ from α,α-dihydroxy acetic acid.

[t] The purity was determined by LC–UV/ELS.

TABLE 2A. α-AMINO ACID DERIVATIVES FROM GLYOXYLIC ACID, NITROGEN NUCLEOPHILES, AND BORONIC ACIDS

Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 2A.



glyoxylic acid

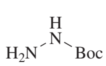
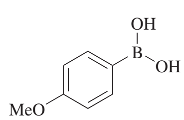
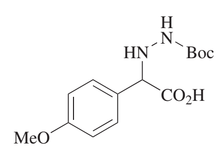
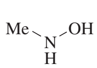
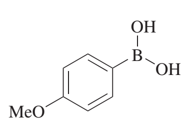
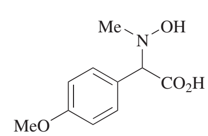
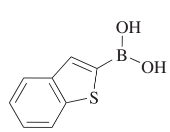
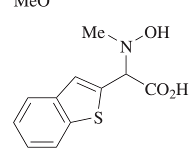
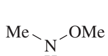
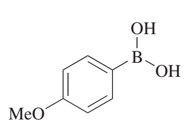
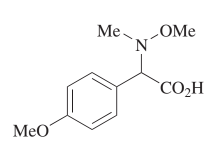
Nitrogen Nucleophile	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_0				
		CH_2Cl_2, rt, 48 h	 (71) (0)[a]	23 104
C_1				
		CH_2Cl_2, rt, 24 h	 (87)	24
		CH_2Cl_2, rt, 24 h	 (79)	24
C_2				
		CH_2Cl_2, rt, 24 h	 (95)	24

TABLE 2A. α-AMINO ACID DERIVATIVES FROM GLYOXYLIC ACID, NITROGEN NUCLEOPHILES, AND BORONIC ACIDS (*Continued*)

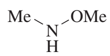
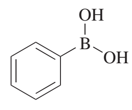
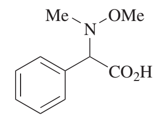
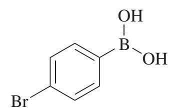
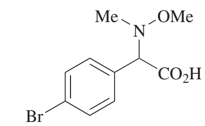
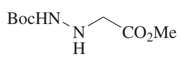
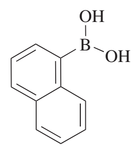
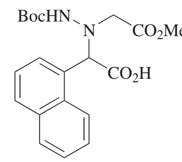
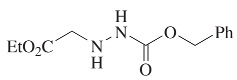
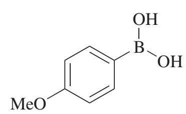
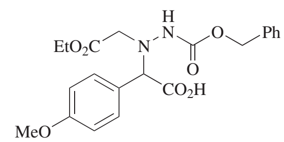
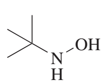
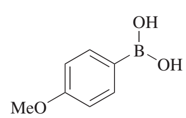
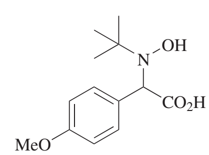
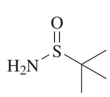
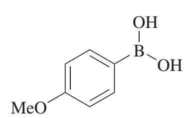
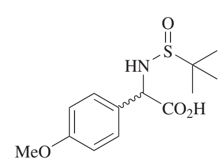
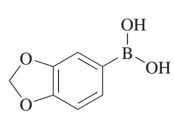
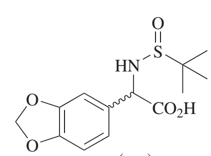
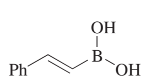
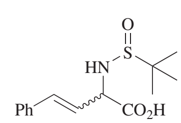
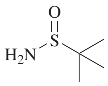
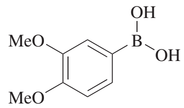
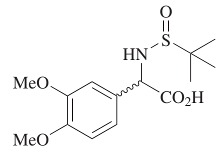
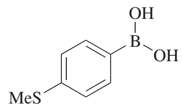
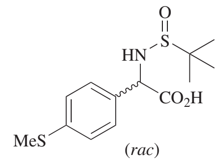
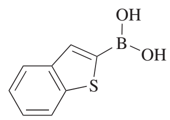
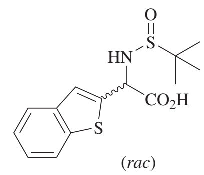
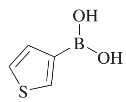
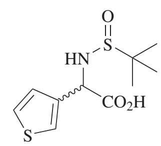
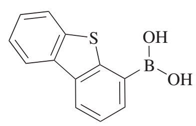
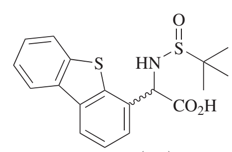
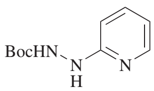
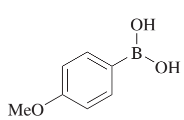
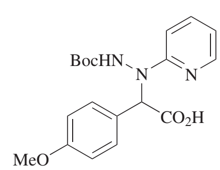
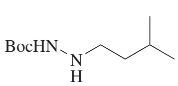
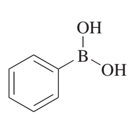
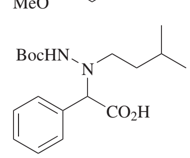
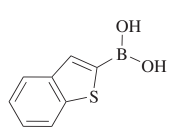
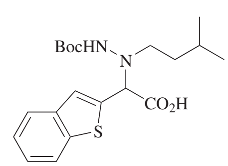
Nitrogen Nucleophile	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 2A.				
C_2				
		CH_2Cl_2, rt, 24 h	 (96)	24
		CH_2Cl_2, rt, 24 h	 (89)	24
		CH_2Cl_2, rt	 Time (h)	
			48 (70)	23
			48 (62)[a]	104
			24 (45)[a]	96
C_3				
		CH_2Cl_2, rt, 48 h	 (60)	23
C_4				
		CH_2Cl_2, rt, 24 h	 (75)[b]	24
		CH_2Cl_2, rt, 48 h	 (*rac*) (72) dr 50:50	24
		CH_2Cl_2, rt, 48 h	 (*rac*) (70) dr 50:50	24
		CH_2Cl_2, rt, 48 h	 (*rac*) (57) dr 50:50	24

TABLE 2A. α-AMINO ACID DERIVATIVES FROM GLYOXYLIC ACID, NITROGEN NUCLEOPHILES, AND BORONIC ACIDS (*Continued*)

Nitrogen Nucleophile	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 2A.				
C_4				
		CH_2Cl_2, rt, 48 h	 (*rac*) (73) dr 50:50	24
		CH_2Cl_2, rt, 48 h	 (*rac*) (50) dr 50:50	24
		CH_2Cl_2, rt, 48 h	 (*rac*) (67) dr 50:50	24
		CH_2Cl_2, rt, 48 h	 (*rac*) (66) dr 50:50	24
		CH_2Cl_2, rt, 48 h	 (*rac*) (68) dr 50:50	24
C_5				
		CH_2Cl_2, rt, 48 h	 (0)	23
		CH_2Cl_2, rt, 48 h	 (89) (47)[a]	23 104
		CH_2Cl_2, rt, 48 h	 (60) (61)[a]	23 104

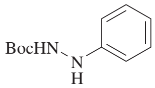
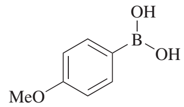
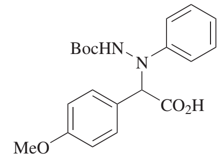
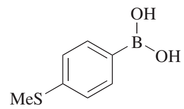
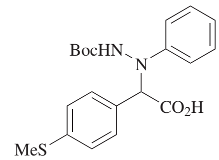
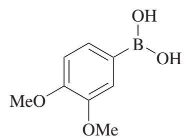
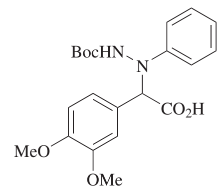
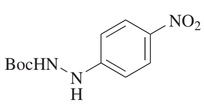
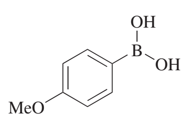
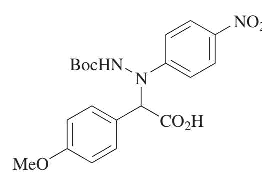
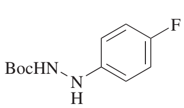
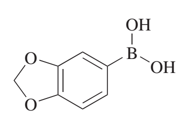
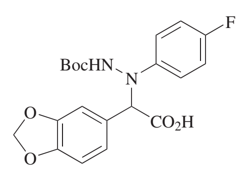
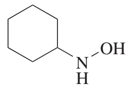
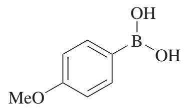
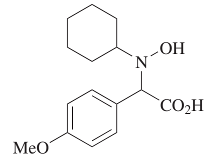
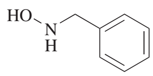
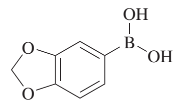
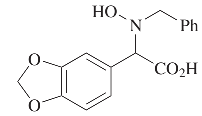
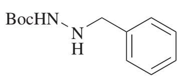
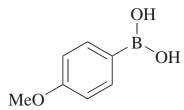
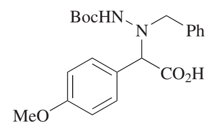
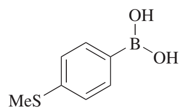
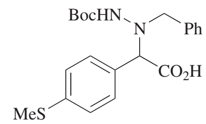
Nitrogen Nucleophile	Boronic Acid	Conditions	Product(s) and Yield(s) (%)		Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 2A.					
C_6					
		CH_2Cl_2, rt		Time (h) 24 (43)[a] 48 (99) 48 (29)[a]	 96 23 104
		CH_2Cl_2, rt, 24 h		(39)[a]	96
		CH_2Cl_2, rt, 24 h		(40)[a]	96
		CH_2Cl_2, rt, 48 h		(34)	23
		CH_2Cl_2, rt, 24 h		(46)[a]	96

TABLE 2A. α-AMINO ACID DERIVATIVES FROM GLYOXYLIC ACID, NITROGEN NUCLEOPHILES, AND BORONIC ACIDS (*Continued*)

Nitrogen Nucleophile	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 2A.				
C_6				
		CH_2Cl_2, rt, 24 h	 (41)[b]	24
C_7				
		CH_2Cl_2, rt, 24 h	 (80)	24
		CH_2Cl_2, rt	 Time (h)	
			48 (86)	23
			48 (39)[a]	25
			48 (79)[a]	104
			24 (42)[a]	96
		CH_2Cl_2, rt, 24 h	 (50)[a]	96

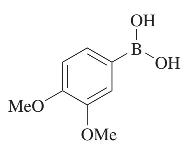
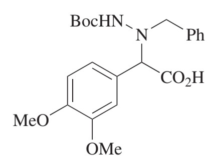
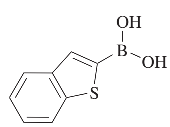
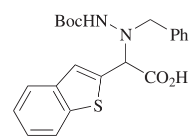
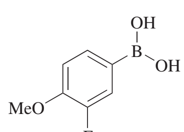
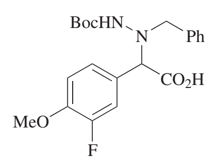
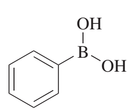
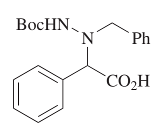
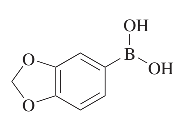
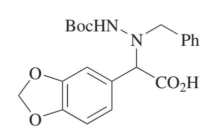
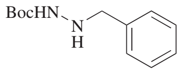
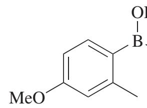
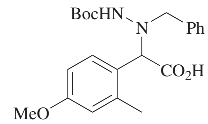
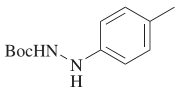
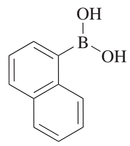
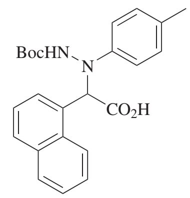
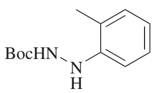
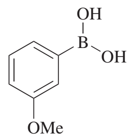
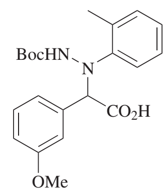
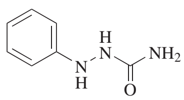
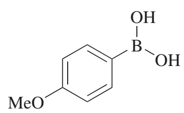
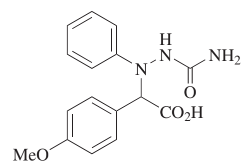
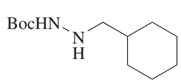
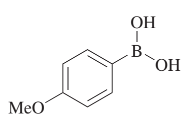
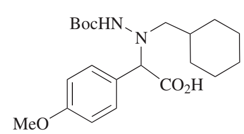
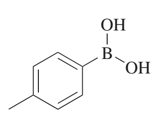
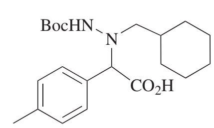
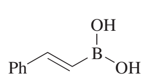
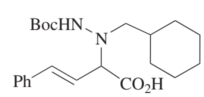
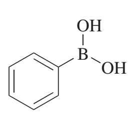
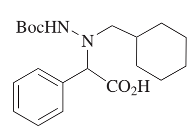
Nitrogen Nucleophile	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt, 24 h	 (45)[a]	96
		CH_2Cl_2, rt, 24 h	 (36)[a]	96
		CH_2Cl_2, rt, 24 h	 (54)[a]	96
		CH_2Cl_2, rt, 24 h	 (25)[a]	96
		CH_2Cl_2, rt, 24 h	 (35)[a]	96

TABLE 2A. α-AMINO ACID DERIVATIVES FROM GLYOXYLIC ACID, NITROGEN NUCLEOPHILES, AND BORONIC ACIDS (*Continued*)

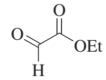
Nitrogen Nucleophile	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
Note: Glyoxylic acid is a coreactant in all of the reactions listed in Table 2A.				
C_7				
		CH_2Cl_2, rt, 24 h	 (27)[a]	96
		CH_2Cl_2, rt, 48 h	 (85) (62)[a]	23 104
		CH_2Cl_2, rt, 24 h	 (44)[a]	96
		CH_2Cl_2, rt, 48 h	 (20)	23
		CH_2Cl_2, rt	 Time (h): 48 (99); 48 (53)[a]; 24 (43)[a]	23 104 96
		CH_2Cl_2, rt, 48 h	 (74)	23
		CH_2Cl_2, rt, 48 h	 (86) (31)[a]	23 104
		CH_2Cl_2, rt, 24 h	 (48)[a]	96

[a] The acutal yield was not reported. This product was used in a multi-step synthesis. The overall yield of the final product was given.

[b] Decomposition was observed.

TABLE 2B. α-AMINO ACID DERIVATIVES FROM ETHYL GLYOXYLATE, AMINES, AND ORGANOBORON REAGENTS

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*
Note: Ethyl glyoxylate is a coreactant in all of the reactions listed in Table 2B.



ethyl glyoxylate

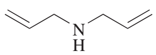
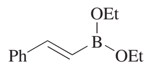
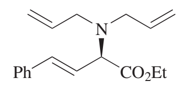
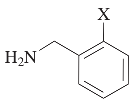
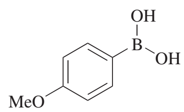
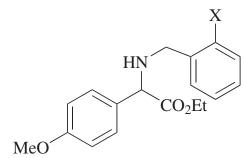
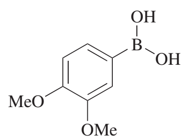
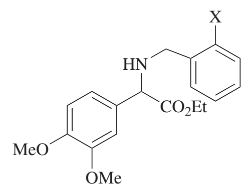
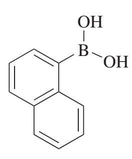
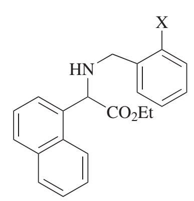
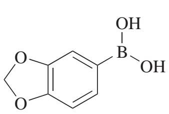
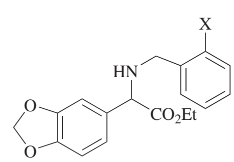
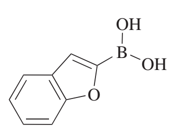
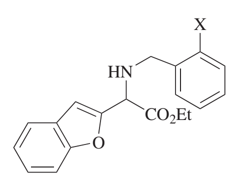
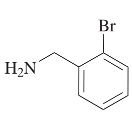
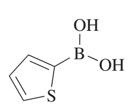
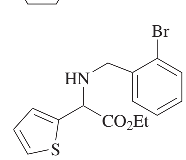
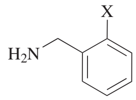
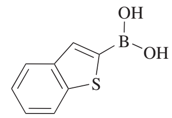
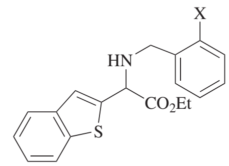
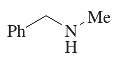
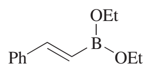
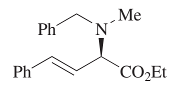
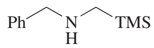
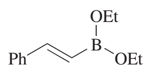
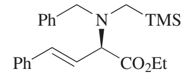
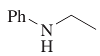
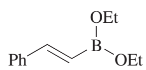
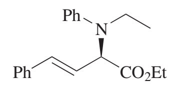
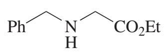
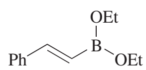
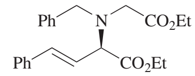
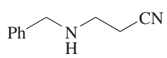
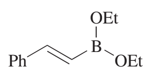
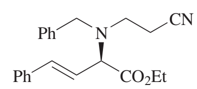
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (87) er 97:3	38
C_7				
		Toluene, 45–50°, 24 h	 X: I (60)[a]; Br (61)[a]	20
		Toluene, 45–50°, 24 h	 X: I (62)[a]; Br (53)[a]	20
		Toluene, 45–50°, 24 h	 X: I (65)[a]; Br (72)[a]	20
		Toluene, 45–50°, 24 h	 X: I (58)[a]; Br (46)[a]	20
		Toluene, 45–50°, 24 h	 X: I (59)[a]; Br (50)[a]	20
		Toluene, 45–50°, 24 h	 (50)[a]	20

TABLE 2B. α-AMINO ACID DERIVATIVES FROM ETHYL GLYOXYLATE, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*
Note: Ethyl glyoxylate is a coreactant in all of the reactions listed in Table 2B.

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Toluene, 45–50°, 24 h	 X: I (54)[a]; Br (50)[a]	20
C_8				
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (81) er 95.0:5.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (84) er 95.5:4.5	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (74) er 89.0:11.0	38
C_9				
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (94) er 95.0:5.0	38
C_{10}				
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (80) er 98.5:1.5	38

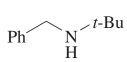
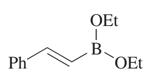
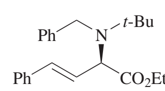
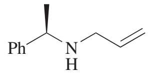
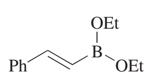
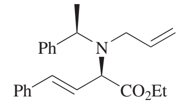
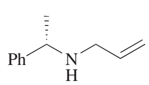
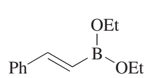
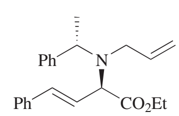
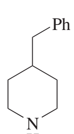
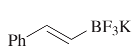
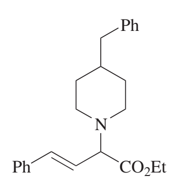
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (73) er 93.0:7.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 major (*R*,*R*) (82) dr 90:10	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 major (*S*,*R*) (89) dr 84:16	38
C_{12}				
		1. Aldehyde, amine, toluene, rt, 10 min 2. RBF_3K, $BF_3•OEt_2$ rt, 1 min; then 90°,1 h	 (21)	48

TABLE 2B. α-AMINO ACID DERIVATIVES FROM ETHYL GLYOXYLATE, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*
Note: Ethyl glyoxylate is a coreactant in all of the reactions listed in Table 2B.

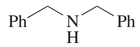
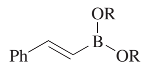
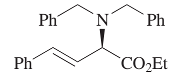
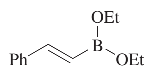
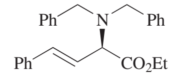
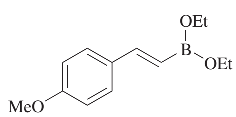
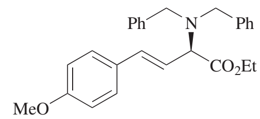
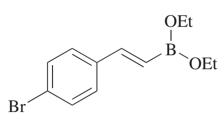
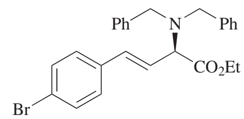
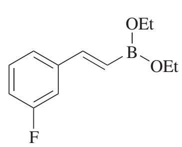
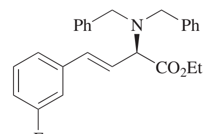
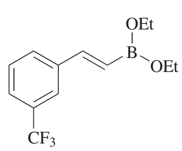
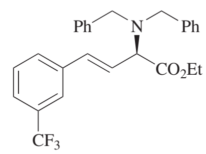
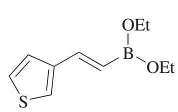
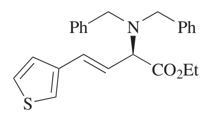
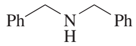
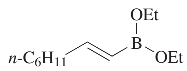
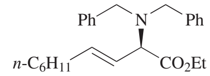
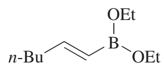
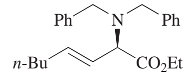
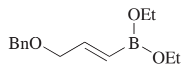
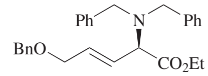
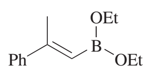
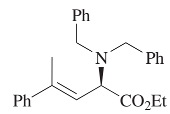
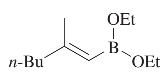
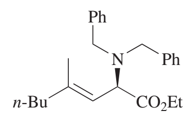
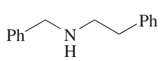
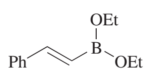
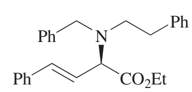
Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
		Catalyst (20 mol %), 3 Å MS, toluene, –15°, 24 h	 R / Catalyst / / er H — (80) — *i*-Pr — (<5) — *i*-Pr **1a** (45) 60.0:40.0 *i*-Pr **1b** (65) 75.0:25.0 *i*-Pr **1c** (51) 70.0:30.0 *i*-Pr **1d** (25) 59.0:41.0 *i*-Pr **1e** (70) 55.0:45.0 *i*-Pr **2a** (60) 70.0:30.0 *i*-Pr **2b** (43) 64.0:36.0 *i*-Pr **2c** (67) 72.0:28.0 *i*-Pr **3** (77) 85.0:15.0 *i*-Pr **4** (80) 87.0:13.0 Me **4** (90) 90.0:10.0 Et **4** (81) 95.5:4.5 *n*-Bu **4** (77) 93.0:7.0 H **4** (99) 57.0:43.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (81) er 95.5:4.5	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (84) er 96.0:4.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (82) er 95.0:5.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (80) er 95.0:5.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (82) er 95.0:5.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (87) er 95.0:5.0	38

TABLE 2B. α-AMINO ACID DERIVATIVES FROM ETHYL GLYOXYLATE, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the ***bold*** *numbers.*

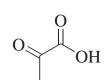
Note: Ethyl glyoxylate is a coreactant in all of the reactions listed in Table 2B.

Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (76) er 97.0:3.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (73) er 95.0:5.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (74) er 95.5:4.5	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (78) er 95.5:5.0	38
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (71) er 93.0:7.0	38
C_{15}				
		(*S*)-VAPOL (**4**, 15 mol %), 3 Å MS, toluene, –15°, 36 h	 (82) er 97.0:3.0	38

[a] The acutal yield was not reported. This product was used in a multi-step synthesis. The overall yield of the final product was given.

TABLE 2C. α-AMINO ACID DERIVATIVES FROM 2-OXOPROPANOIC ACID, AMINES, AND BORONIC ACIDS

Note: 2-Oxopropanoic acid is a coreactant in all of the reactions listed in Table 2C.



2-oxopropanoic acid

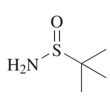
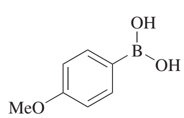
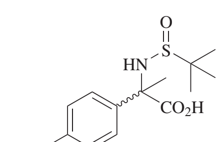
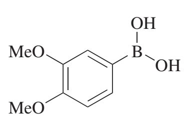
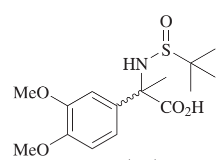
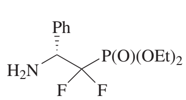
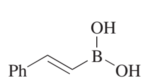
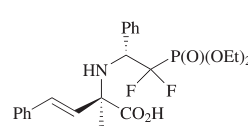
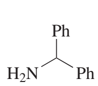
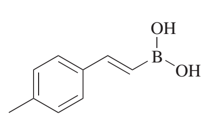
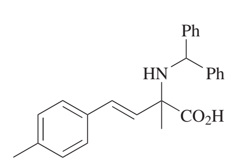
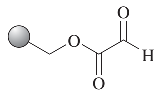
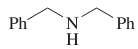
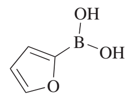
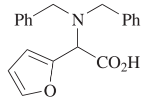
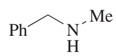
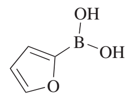
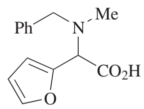
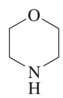
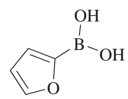
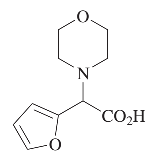
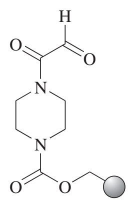
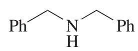
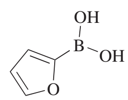
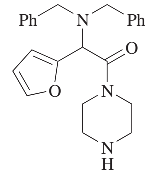
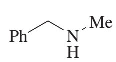
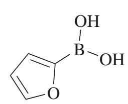
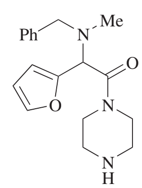
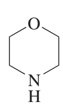
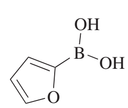
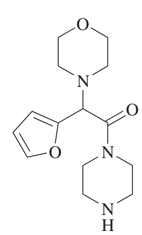
Amine	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		CH_2Cl_2, rt, 48 h	 (*rac*) (37) dr 50:50	24
		CH_2Cl_2, rt, 48 h	 (*rac*) (39) dr 50:50	24
C_8				
		CH_2Cl_2, rt, 48 h	 major (*R*,*R*) (49) dr 75:25	92
C_{13}				
		CH_2Cl_2, rt, 12-48 h	 (76)	33

TABLE 2D. α-AMINO ACID DERIVATIVES FROM POLYMER-SUPPORTED 2-OXOACETIC ACID DERIVATIVES, AMINES, AND BORONIC ACIDS

HCOCOY	Amine and Boronic Acid		Conditions	Product(s) and Yield(s) (%)		Refs.
C_2						
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(21) 70% pure [a]	13
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(17) 59% pure [a]	13
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(15) — pure [a]	13
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(37) 77% pure [b]	13
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(17) 90% pure [b]	13
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(27) — pure [b]	13

[a] The yield was determined by ^{1}H NMR using DMSO-d_5 as the internal standard, based on the theoretical loading of Wang aldehyde resin (2.45 mmol/g). The symbol "—" means that the purity was not determined. See comments in Ref. 20 in the original paper.

[b] The yield was determined by ^{1}H NMR using DMSO-d_5 as the internal standard, based on the theoretical loading of Wang aldehyde resin (1.04 mmol/g). The symbol "—" means that the purity was not determined. See comments in Ref. 20 in the original paper.

TABLE 2E. α-AMINO ACID DERIVATIVES FROM $RCOCO_2Me$ (R = Me, Ph), AMMONIA, AND BORONIC ACIDS

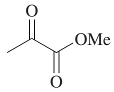
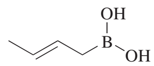
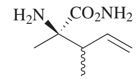
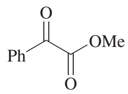
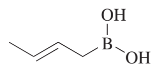
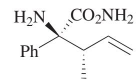
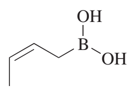
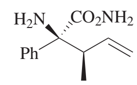
$RCOCO_2Me$	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		NH_3, MeOH, rt, 24 h	 (88) dr 60:40	29
C_8				
		NH_3, MeOH, rt, 24 h	 major (*rac*) (95) dr 97:3	29
		NH_3, MeOH, rt, 24 h	 major (*rac*) (92) dr 96:4	29

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS

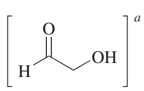
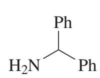
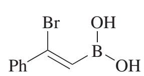
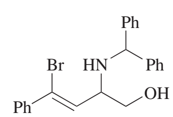
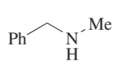
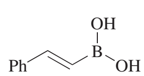
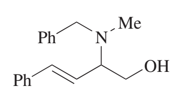
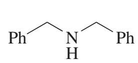
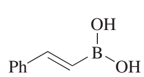
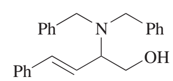
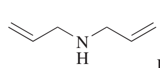
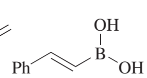
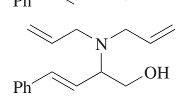
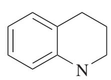
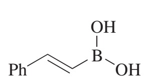
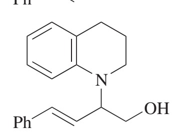
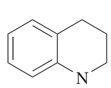
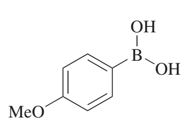
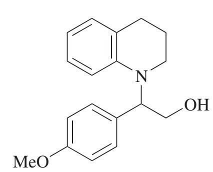
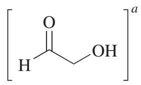
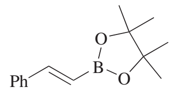
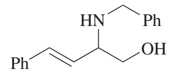
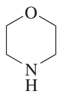
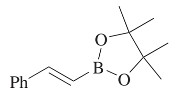
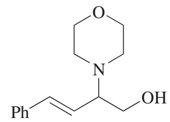
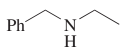
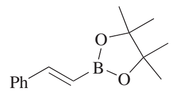
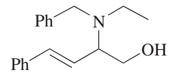
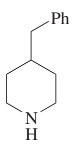
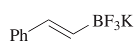
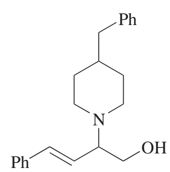
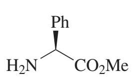
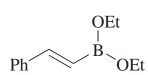
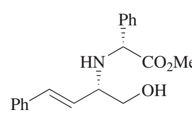
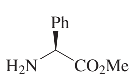
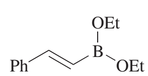
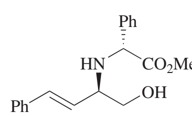
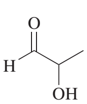
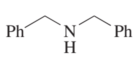
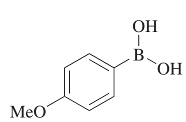
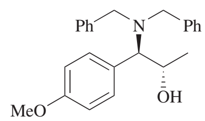
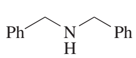
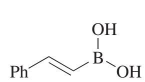
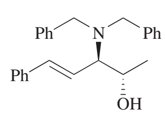
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*					
C_2					
 [a]			EtOH, rt, 24 h	 (87)	39
			Solvent, rt	 Solvent Time (h) EtOH 24 (84) H_2O 48 (62)	39 56
			H_2O, rt, 48 h	 (64)	56
			H_2O, rt, 48 h	 (69)	56
			H_2O, 50°, 24 h	 (75)	56
			H_2O, 50°, 48 h	 (74)	56

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
 [a]	 	Solvent, rt, 4 h	 Solvent: MeOH (78); HFIP (46)	21
	 	See table.		21
	 	See table.		21
	 	1. Aldehyde, amine, toluene, rt, 10 min 2. RBF_3K, BF_3•OEt_2 rt, 1 min; then 90°, 1 h	 (78)	48
	 	4 Å MS, $PhCF_3$, rt		105
	 	Cat. **6** (20 mol %)[c], 4 Å MS, $PhCF_3$, rt	 (75) dr 10:1 (*S*,*R*)/(*S*,*S*)	105
C_3				
	 	EtOH, rt, 24 h	 major (*rac*) (63) dr >99.5:0.5	39
	 	EtOH, rt, 24 h	 major (*rac*) (84) dr >99.5:0.5	39

Morpholine entry:

	Solvent	Temp	Time	
MW, 300 W	MeOH	120°	10 min	(81)
—	HFIP	rt	4 h	(96)

N-Ethylbenzylamine entry:

	Solvent	Temp	Time	
MW, 300 W	MeOH	120°	10 min	(75)
—	HFIP	rt	4 h	(99)

Phenylglycine methyl ester entry (4 Å MS, $PhCF_3$, rt):

Catalyst	Yield[b]	dr (*S*,*S*)/(*S*,*R*)
—	(81)	4:1
1b (20 mol %)[c]	(83)	20:1

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

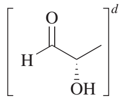
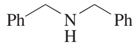
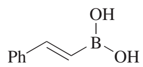
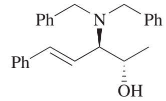
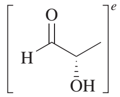
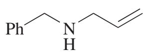
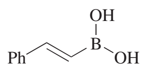
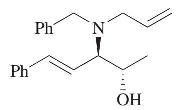
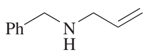
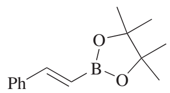
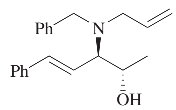
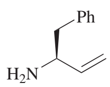
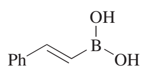
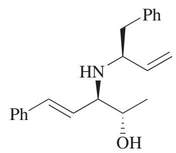
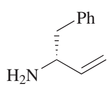
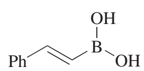
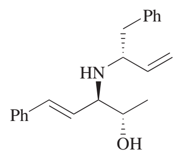
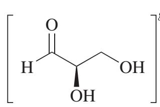
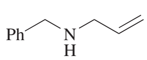
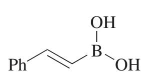
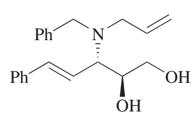
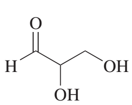
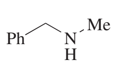
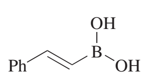
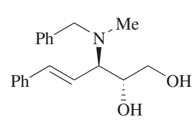
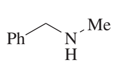
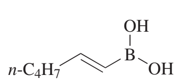
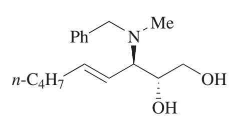
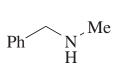
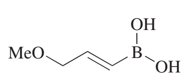
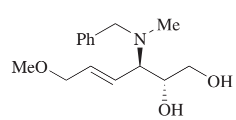
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_3						
 [d]			EtOH, rt, 24 h	 major	(85) dr >99.5:0.5 er >99.5:0.5	39
 [e]			EtOH, reflux, 16 h		(83) dr >99.5:0.5 er >99.5:0.5	106
			EtOH, reflux, 5 h		(62) dr >99.5:0.5 er >99.5:0.5	106
			EtOH, reflux, 24 h		(76) dr >99.5:0.5 er >99.5:0.5	106
			EtOH, reflux, 16 h		(—)[f] dr >99.5:0.5 er >99.5:0.5	106
 [g]			EtOH, reflux, 16 h		(77) dr >99.5:05 er >99.5:0.5	106
			EtOH, rt, 24 h	 major (*rac*)	(87) dr >99.5:05	39
			EtOH, rt, 24 h	 major (*rac*)	(73) dr >99.5:0.5	39
			EtOH, rt, 24 h	 major (*rac*)	(67) dr >99.5:0.5	39

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

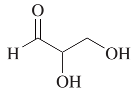
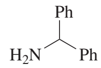
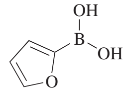
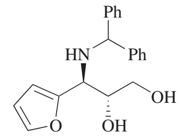
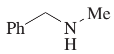
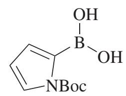
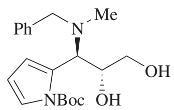
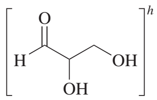
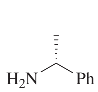
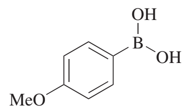
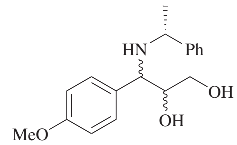
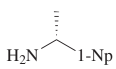
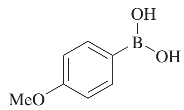
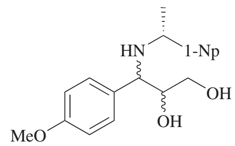
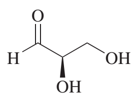
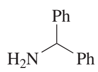
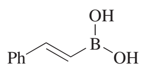
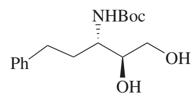
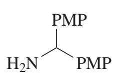
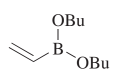
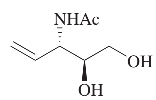
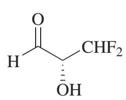
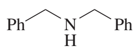
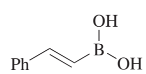
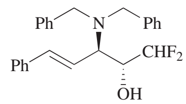
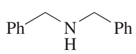
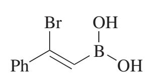
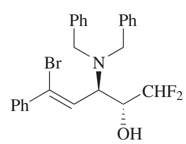
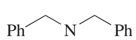
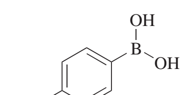
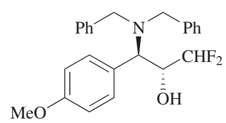
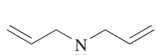
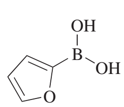
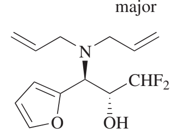
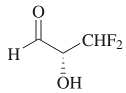
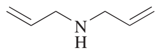
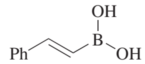
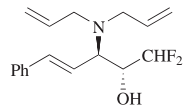
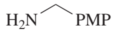
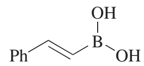
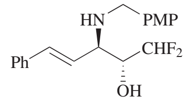
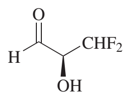
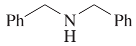
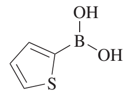
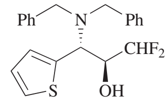
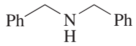
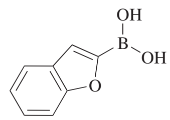
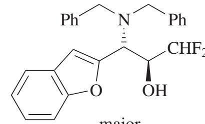
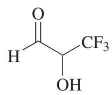
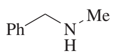
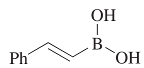
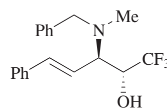
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*						
C_3						
			EtOH, rt, 24 h	 major (*rac*)	(86) dr >99.5:0.5	39
			EtOH, rt, 24 h	 major (*rac*)	(73) dr >99.5:0.5	39
			EtOH, rt, 72 h		(56) dr ~1:1 (*anti*/*anti*)	107
			EtOH, reflux, 72 h		(50) dr 53:47 (*anti*/*anti*)	107
			1. EtOH, rt, 24 h 2. H_2, Pd/C 3. $(Boc)_2O$, Et_3N	 major	(70) dr >99.5:0.5 er >99.5:0.5	39
			1. $EtOH/H_2O$ (4:1), 50°, 72 h 2. TFA, 50° 3. Ac_2O, MeOH	 major	(60) dr >99.5:0.5	41
			EtOH, rt, 24–48 h	 major	(60) dr >99.5:0.5 er >99.5:0.5	108
			EtOH, rt, 24–48 h	 major	(63) dr >99.5:0.5 er 97.0:3.0	108
			EtOH, rt, 24–48 h	 major	(55) dr >99.5:0.5 er 96.0:4.0	108
			EtOH, rt, 24–48 h	 major	(90) dr >99.5:0.5 er 93.0:7.0	108

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 	EtOH, rt, 24–48 h	 major (75) dr >99.5:0.5 er 96.0:4.0	108
	 	EtOH, rt, 24–48 h	 major (30) dr >99.5:0.5 er 98.0:2.0	108
	 	EtOH, rt, 24–48 h	 major (57) dr >99.5:0.5 er 96.0:4.0	108
	 	EtOH, rt, 24–48 h	 major (65) dr >99.5:0.5 er >99.5:0.5	108
	 	EtOH, rt, 24–48 h	 major (*rac*) (75) dr >99.5:0.5	43

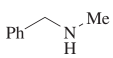
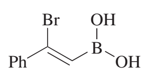
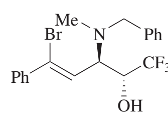
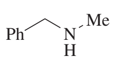
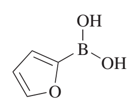
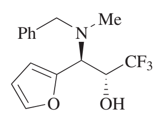
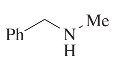
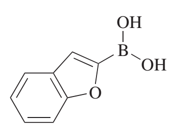
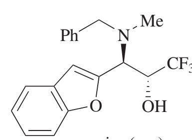
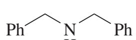
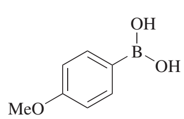
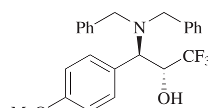
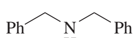
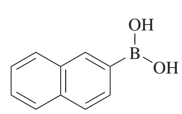
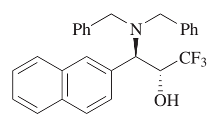
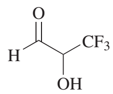
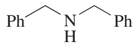
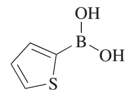
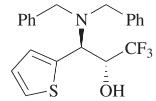
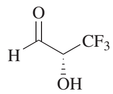
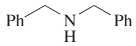
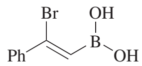
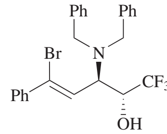
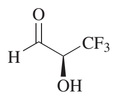
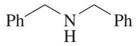
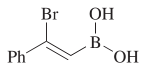
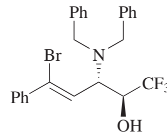
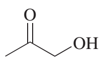
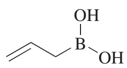
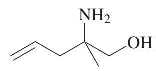
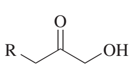
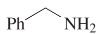
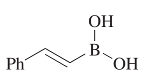
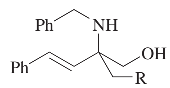
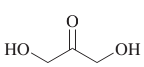
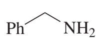
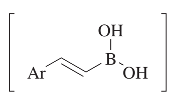
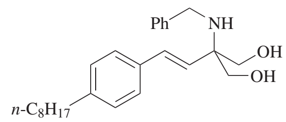
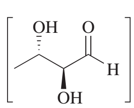
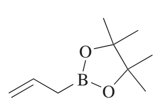
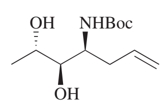
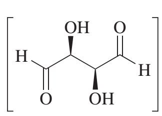
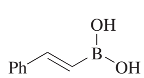
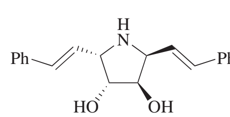
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
	 	EtOH, rt, 24–48 h	 major (*rac*) (80) dr >99.5:0.5	43
	 	EtOH, rt, 24–48 h	 major (*rac*) (85) dr >99.5:0.5	43
	 	EtOH, rt, 24–48 h	 major (*rac*) (75) dr >99.5:0.5	43
	 	EtOH, rt, 24–48 h	 major (*rac*) (70) dr >99.5:0.5	43
	 	EtOH, rt, 24–48 h	 major (*rac*) (73) dr >99.5:0.5	43

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

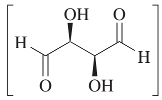
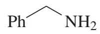
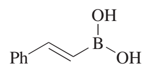
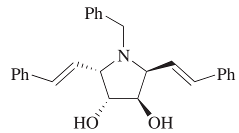
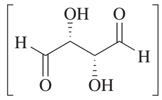
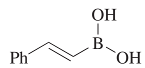
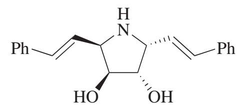
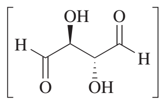
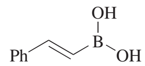
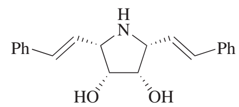
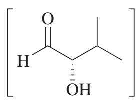
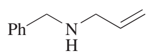
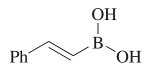
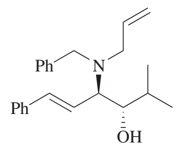
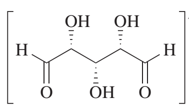
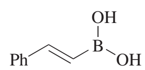
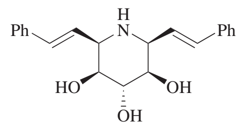
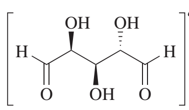
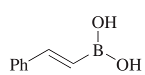
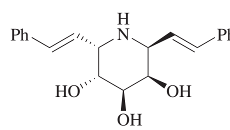
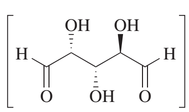
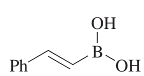
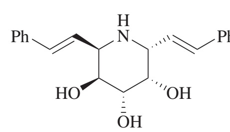
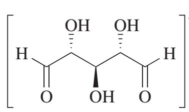
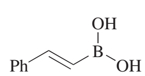
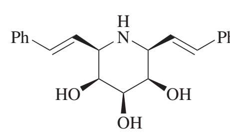
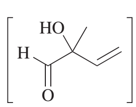
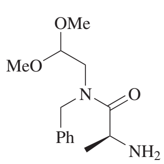
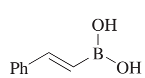
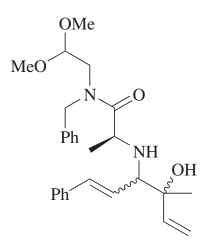
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 	EtOH, rt, 24–48 h	 major (*rac*) (67) dr >99.5:0.5	43
 er = *x*	 	Solvent(s), rt, 24–48 h		43
 er 98.0:2.0	 	MeOH/CH_2Cl_2 (1:4), rt, 24–48 h	 (79) er 96.0:4.0	43
	NH_3 	MeOH, rt, 16 h	 (80)	29
	 	EtOH, rt, 24 h	 R: OH (40); H (—)[i]	42
	  [j] Ar = 4-n-$C_8H_{17}C_6H_4$	EtOH, rt, 36 h	 (44)[j]	42
C_4				
 [k]	NH_3 	1. Aldehyde, NH_3, EtOH, 0°, 1 h 2. Boronate, 0°, 24 h 3. Boc_2O, CH_2Cl_2, rt, 4 h	 major (51) dr >99:1	28
 [l]	NH_3 	MeOH, rt, 72 h	 major (70) dr >99:1	40

x	Solvent(s)		er
91.0:9.0	MeOH/CH_2Cl_2 (1:1)	(—)	77.5:22.5
88.5:11.5	MeOH	(—)	65.0:35.0
92.5:7.5	MeOH/CH_2Cl_2 (1:4)	(71)	92.5:7.5

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
 [l]	 	MeOH, rt, 72 h	 (65)	40
 [m]	NH_3 	MeOH, rt, 72 h	 (70)	40
 [n] (*meso*)	NH_3 	MeOH, rt, 72 h	 (70)	40
C_5				
 [o]	 	EtOH, rt, 40 h	 (61), dr >99.5:0.5 er >95.5:0.5	106
 [p] (*meso*)	NH_3 	MeOH, rt, 72 h	 (65)	40
 [q]	NH_3 	MeOH, rt, 72 h	 (60)	40
 [r]	NH_3 	MeOH, rt, 72 h	 (55)	40
 [s] (*meso*)	NH_3 	MeOH, rt, 72 h	 (65)	40
 [t]	 	MeOH/H_2O (1:1), 50°, 24 h	 (82)	109

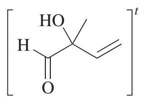
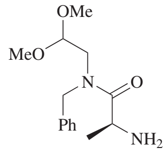
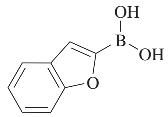
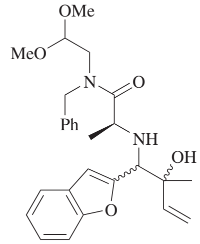
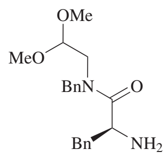
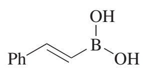
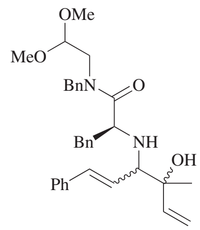
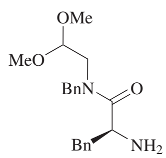
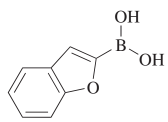
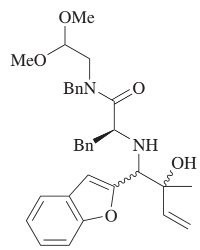
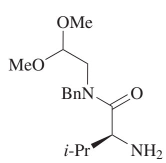
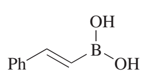
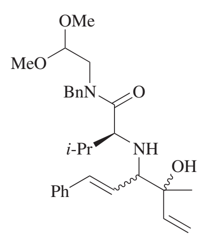
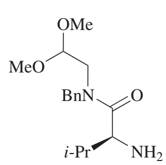
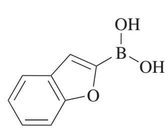
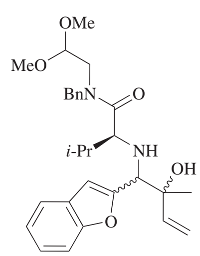
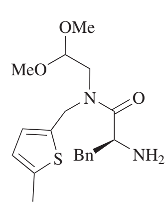
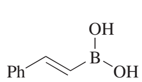
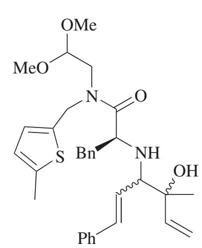
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*				
C_5 	 	MeOH/H_2O (1:1), 50°, 24 h	 (93)	109
	 	MeOH/H_2O (1:1), 50°, 24 h	 (90)	109
	 	MeOH/H_2O (1:1), 50°, 24 h	 (95)	109
	 	MeOH/H_2O (1:1), 50°, 24 h	 (89)	109
	 	MeOH/H_2O (1:1), 50°, 24 h	 (93)	109
	 	MeOH/H_2O (1:1), 50°, 24 h	 (87)	109

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

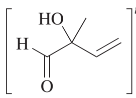
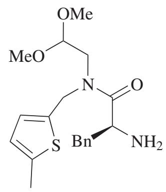
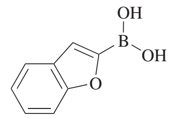
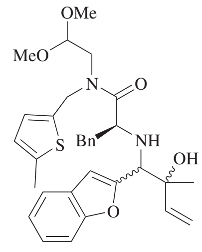
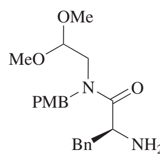
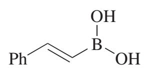
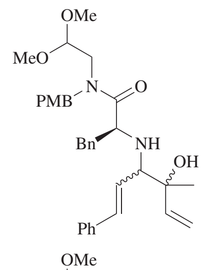
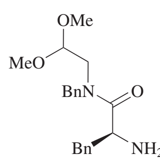
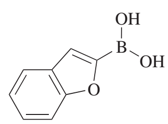
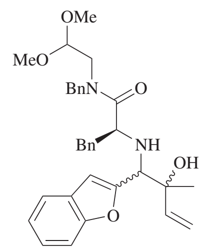
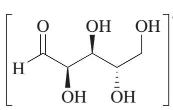
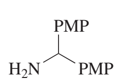
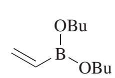
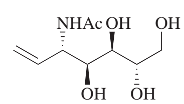
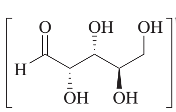
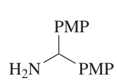
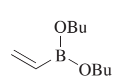
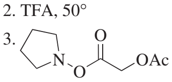
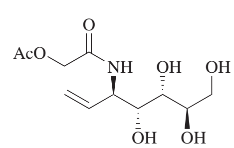
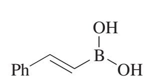
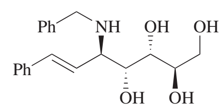
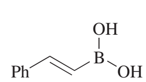
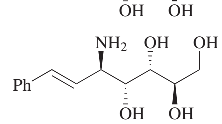
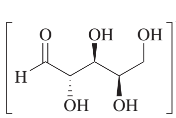
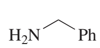
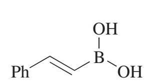
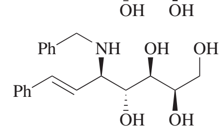
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
 t	 	MeOH/H_2O (1:1), 50°, 24 h	 (96)	109
	 	MeOH/H_2O (1:1), 50°, 24 h	 (91)	109
	 	MeOH/H_2O (1:1), 50°, 24 h	 (95)	109
 u	 	1. EtOH/H_2O (4:1), 50°, 72 h 2. TFA, 50° 3. Ac_2O, MeOH	 major (55) dr >99.5:0.5	41
 v	 	1. EtOH/H_2O (4:1), 50°, 72 h 2. TFA, 50° 3. 	 major (50) dr >99.5:0.5	41
	 	—	 (90)	40
	NH_3 	—	 (0)	40
 w	 	EtOH, rt, 72 h	 (82)	69

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

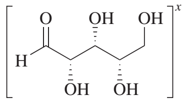
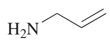
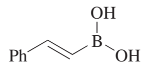
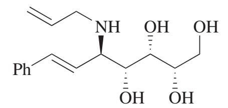
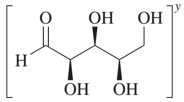
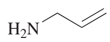
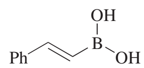
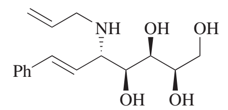
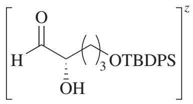
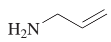
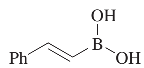
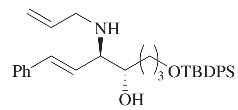
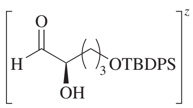
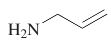
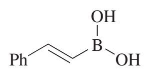
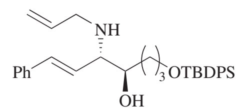
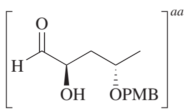
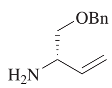
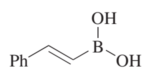
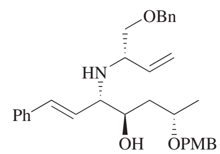
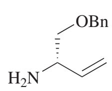
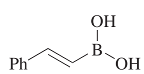
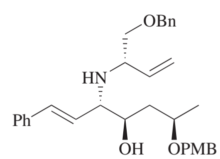
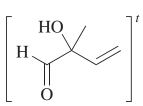
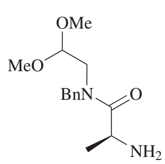
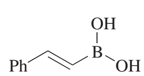
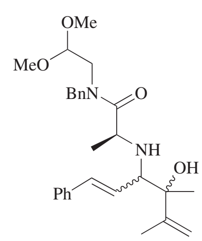
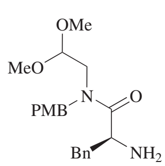
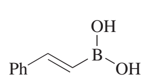
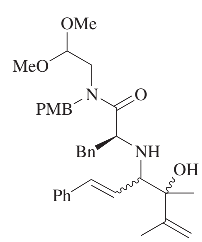
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_5						
			EtOH, rt		Time (h): 16 (73) 16 (73) 72 (92)	65 68 67
			EtOH, rt, 72 h		(91)	66
			CH_2Cl_2, rt, 40 h		(35)[z] er 91.5:8.5	15
			CH_2Cl_2, rt, 40 h		(38)[z] er 96.5:3.5	15
			CH_2Cl_2, rt, 48 h		(53)[aa]	44
			CH_2Cl_2, rt, 48 h		(40)[aa]	44
			MeOH/H_2O (1:1), 50°, 24 h		(87)	109
			MeOH/H_2O (1:1), 50°, 24 h		(90)	109

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

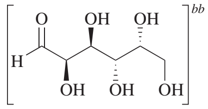
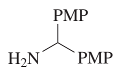
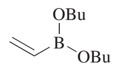
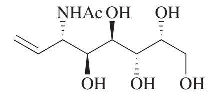
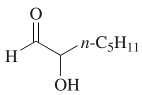
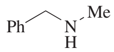
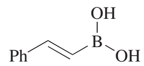
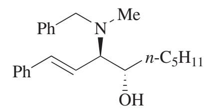
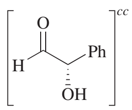
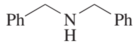
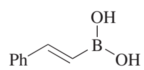
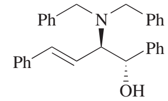
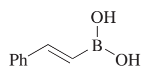
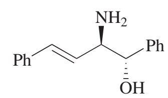
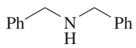
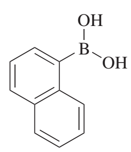
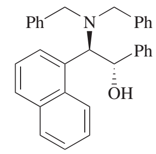
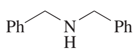
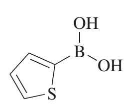
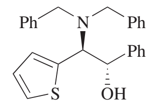
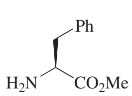
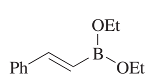
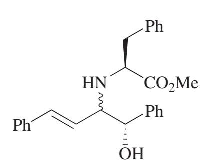
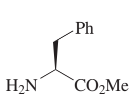
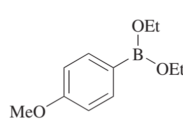
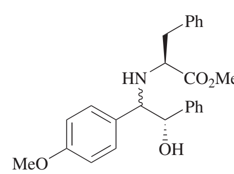
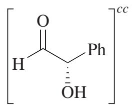
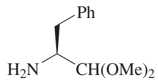
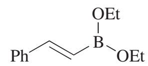
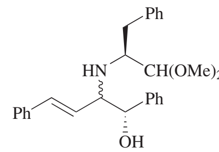
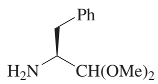
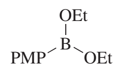
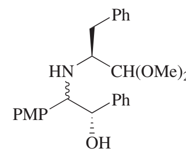
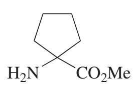
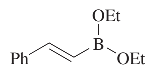
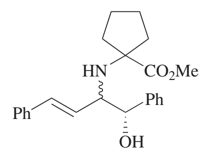
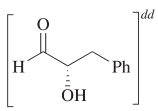
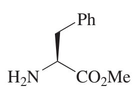
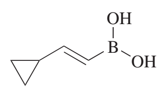
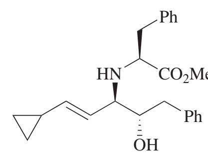
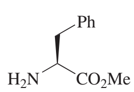
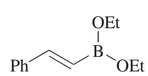
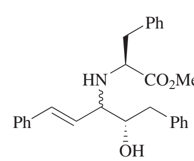
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*						
C_6						
 [bb]			1. EtOH/H_2O (4:1), 50°, 72 h 2. TFA, 50° 3. Ac_2O, MeOH	 major	(50) dr >99.5:0.5	41
C_7						
			EtOH, rt, 24 h	 major (*rac*)	(84) dr >99.5:0.5	39
C_8						
 [cc]			EtOH, rt, 24 h	 major	(88) dr >99.5:0.5 er >99.5:0.5	39
	NH_3		EtOH, rt, 24 h	 major	(39) dr >99.5:0.5 er >99.5:0.5	39
			EtOH, rt, 24 h	 major	(84) dr >99.5:0.5 er >99.5:0.5	39
			EtOH, rt, 24 h	 major	(86) dr >99.5:0.5 er >99.5:0.5	39
			Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt		(95) (80)[b] dr 5.5:1 (*syn*/*anti*)	105
			Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt		(75)[b] dr 4:1 (*syn*/*anti*)	105

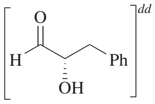
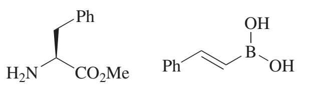
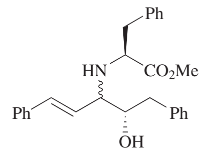
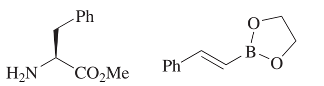
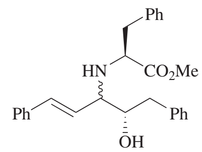
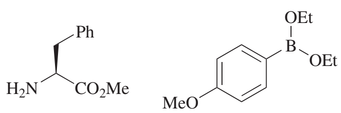
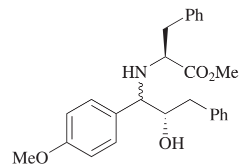
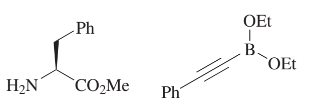
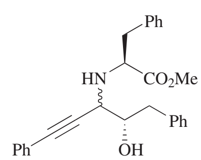
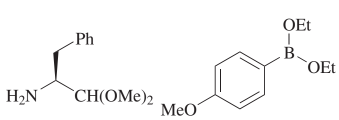
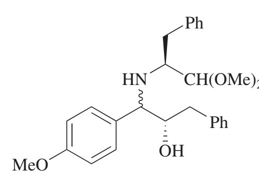
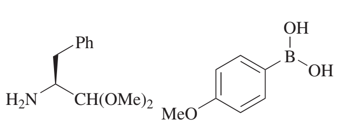
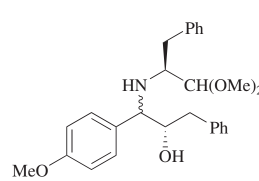
TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8  [cc]	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (96) (84)[b] dr 7:1 (*syn*/*anti*)	105
	 	Cat. **6** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (70)[b] dr 1:10 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (71) (40) dr 1.5:1 (*syn*/*anti*)	105
C_9  [dd]	 	EtOH, rt	 major (85) dr >99.5:0.5	110
	 	Catalyst (20 mol %),[c] solvent, rt		105

Solvent	Catalyst[c]		dr (*syn*/*anti*)[ee]
$PhCF_3$	—	(24)	*anti* only
$PhCF_3$	**4**	(69)	1:10
$PhCF_3$	**5a**	(73)	1:6
$PhCF_3$	**5b**	(66)	1:8
$PhCF_3$	**1a**	(41)	1:4
$PhCF_3$	**1f**	(81)	2:3
$PhCF_3$	**1b**	(70)	4:1
$PhCF_3$	**1b**	(68) (54)	5.5:1[ff]
toluene	**1b**	(67)	1:1
CH_2Cl_2	**1b**	(57)	1:3
THF	**1b**	(<5)	—[f]
$PhCF_3$	**6**	(86)	*anti* only
$PhCF_3$	*rac*-(**1b** & **6**)	(84)	1:9

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*				
C_9  [dd]		Cat. **1b** (20 mol %),[c] $PhCF_3$, rt	 (48) dr 1:1.5 (*syn*/*anti*)	105
		Cat. **1b** (20 mol %),[c] $PhCF_3$, rt	 (<5) dr —[f]	105
		Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (62) dr 5:1 (*syn*/*anti*)	105
		Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (77) dr 5:1 (*syn*/*anti*)	105
		Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (65) dr 1:1 (*syn*/*anti*)	105
		CH_2Cl_2, rt	 (79) dr 94:6 (*anti*/*syn*)	111

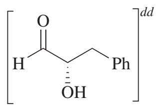
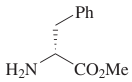
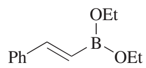
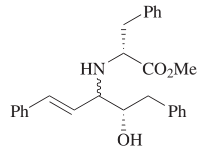
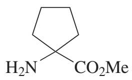
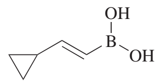
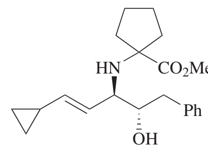
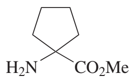
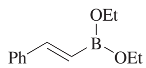
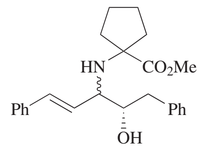
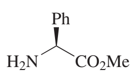
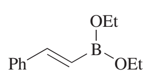
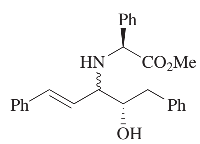
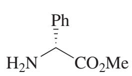
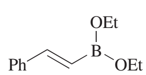
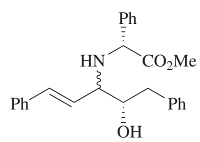
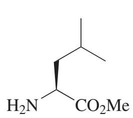
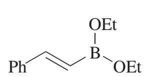
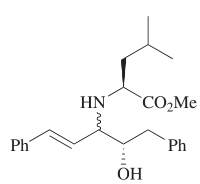
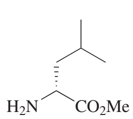
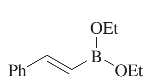
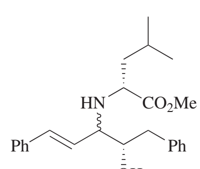
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*				
C_9				
 [dd]	 	Cat. **6** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (61) dr 1:3 (*syn*/*anti*)	105
	 	CH_2Cl_2/HFIP (9:1), rt	 major (84) dr >99.5:0.5	110
	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (70) (45) dr 2:1 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (55) dr 2:1 (*syn*/*anti*)	105
	 	Cat. **6** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (57) dr 1:20 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (80) (56) dr 7.5:1 (*syn*/*anti*)	105
	 	Cat. **6** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (71) dr 1:2 (*syn*/*anti*)	105

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

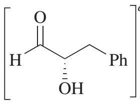
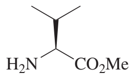
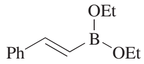
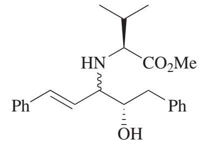
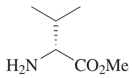
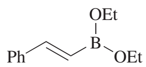
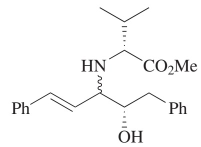
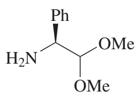
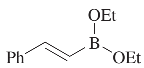
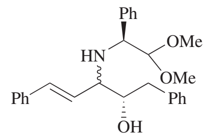
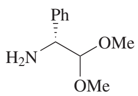
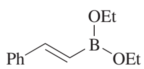
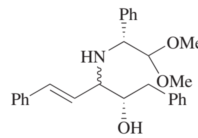
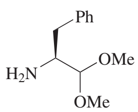
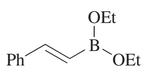
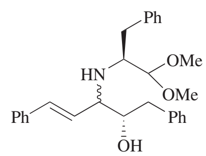
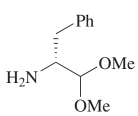
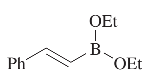
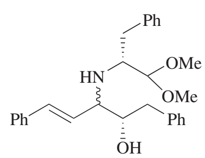
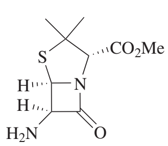
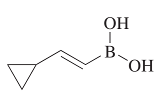
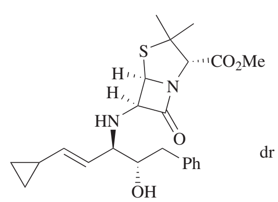
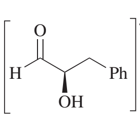
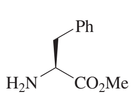
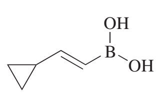
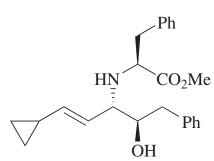
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
 [dd]	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (65) dr 2.5:1 (*syn*/*anti*)	105
	 	Cat. **6** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (68) dr 1:6 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (72) (48)[b] dr 2:1 (*syn*/*anti*)	105
	 	Cat. **6** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (74) dr 1:10 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (94) (80)[b] dr 6:1 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %),[c] 4 Å MS, $PhCF_3$, rt	 (83) (38)[b] dr 4:1 (*syn*/*anti*)	105
	 	CH_2Cl_2/HFIP (9:1), rt	 major (83) dr >99.5:0.5	110
 [gg]	 	EtOH, rt	 major (83) dr >99.5:0.5	110

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

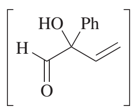
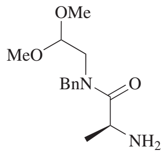
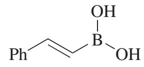
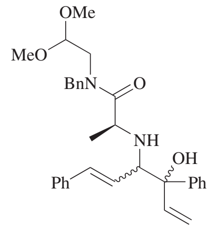
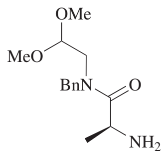
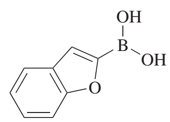
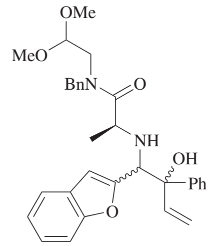
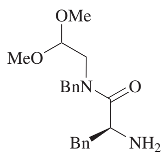
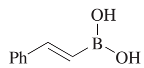
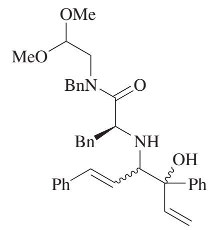
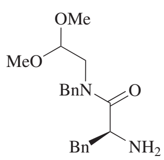
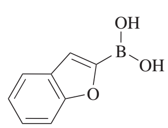
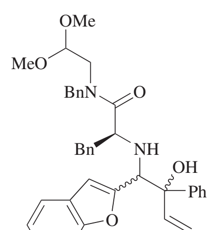
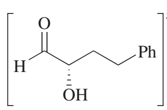
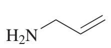
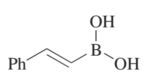
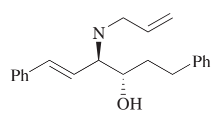
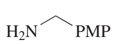
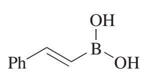
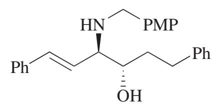
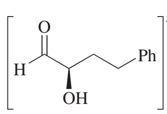
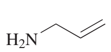
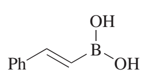
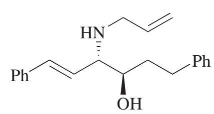
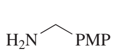
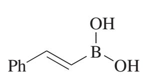
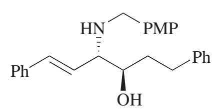
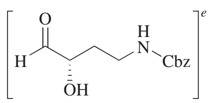
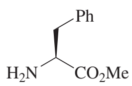
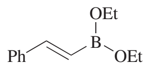
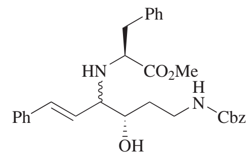
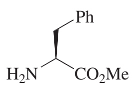
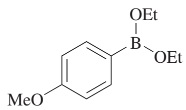
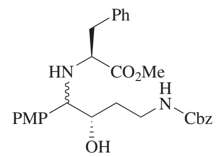
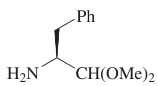
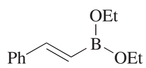
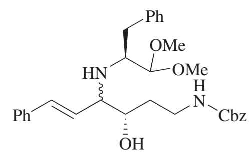
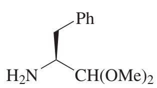
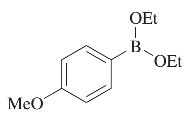
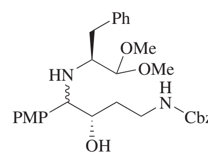
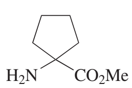
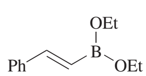
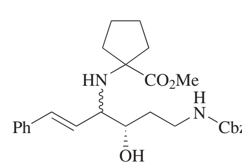
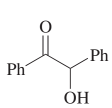
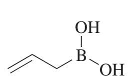
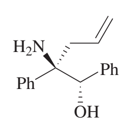
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*						
C_{10}  [t]			MeOH/H_2O (1:1), 50°, 24 h		(88)	109
			MeOH/H_2O (1:1), 50°, 24 h		(94)	109
			MeOH/H_2O (1:1), 50°, 24 h		(83)	109
			MeOH/H_2O (1:1), 50°, 24 h		(89)	109
 [z]			CH_2Cl_2, rt, 40 h		(44)[z] er 95.5:4.5	15
			CH_2Cl_2, rt, 40 h		(46)[z] er 95.5:4.5	15
 [z]			CH_2Cl_2, rt, 40 h		(51)[z] er 97.0:3.0	15
			CH_2Cl_2, rt, 40 h		(43)[z] er 97.5:2.5	15

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to Chart 1 preceding the tables for catalyst structures corresponding to the **bold** numbers.*				
C_4				
 [e]	 	Cat. **1b** (20 mol %)[c], 4 Å MS, $PhCF_3$, rt	 (84) (56)[b] dr 2:1 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %)[c], 4 Å MS, $PhCF_3$, rt	 (73) dr 2:1 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %)[c], 4 Å MS, $PhCF_3$, rt	 (77) (45)[b] dr 1.5:1 (*syn*/*anti*)	105
	 	Cat. **6** (20 mol %)[c], 4 Å MS, $PhCF_3$, rt	 (71) dr 1:4 (*syn*/*anti*)	105
	 	Cat. **1b** (20 mol %)[c], 4 Å MS, $PhCF_3$, rt	 (69) (33) dr 1:1 (*syn*/*anti*)	105
C_{14}				
	NH_3 	MeOH, rt, 16 h	 major (*rac*) (81) dr 88:12	29

[a] The starting 2-hydroxyacetaldehyde exists in solution as the dimeric 1,4-dioxane-2,5-diol.

[b] This value is the yield of the diastereomeric mixture upon isolation. The yield given in the second parenthesis is the yield of the isolated *syn* diastereomer (dr >20:1).

[c] Please refer to Chart 1 for the structures of catalysts.

[d] The starting (2*S*)-2-hydroxypropanal was generated in situ from (5*S*)-2,2,5-trimethyl-1,3-dioxolan-4-ol.

[e] The starting (2*S*)-2-hydroxypropanal was generated in situ from *O*-TBDPS-protected hydroxypropanal.

[f] The value was not determined.

[g] The starting (2*R*)-2,3-dihydroxypropanal was generated in situ from (*R*)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde.

[h] The starting 2,3-dihydroxypropanal exists as the dimeric DL-glyceraldehyde.

[i] The product was not obtained.

[j] The organoboron reagent was generated in situ from 1-ethynyl-4-octylbenzene and catecholborane. The actual yield was not reported; the overall yield from 1-ethynyl-4-octylbenzene was 44%.

[k] The starting (2*S*,3*S*)-2,3-dihydroxybutanal was generated in situ from L-chinovose.

[l] The starting (2*S*,3*S*)-2,3-dihydroxysuccinaldehyde was generated in situ by $PhI(OAc)_2$ oxidation of 3,4-*O*-isopropylidene-D-mannitol, followed by H_2SO_4 deprotection. The overall yields from 3,4-*O*-isopropylidene-D-mannitol were 70% and 65%, respectively.

[m] The starting (2*R*,3*R*)-2,3-dihydroxysuccinaldehyde was generated in situ by $PhI(OAc)_2$ oxidation of 3,4-*O*-isopropylidene-L-mannitol, followed by H_2SO_4 deprotection.

TABLE 3. 1,2-AMINO ALCOHOLS FROM α-HYDROXY ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.

[n] The starting (*meso*)-2,3-dihydroxysuccinaldehyde was generated in situ by $PhI(OAc)_2$ oxidation of (*meso*)-2,5-dimethoxy-tetrahydro-(3,4)-furandiol, followed by H_2SO_4 deprotection.

[o] The starting (2*S*)-2-hydroxy-3-methylbutanal was generated in situ from *O*-TBDPS-protected hydroxybutanal.

[p] The starting (*meso*)-2,3,4-trihydroxypentanedial was generated in situ by $PhI(OAc)_2$ oxidation of 1,2-*O*-isopropylidene-D-glucose, followed by H_2SO_4 deprotection.

[q] The starting (2*S*,4*S*)-2,3,4-trihydroxypentanedial was generated in situ by $PhI(OAc)_2$ oxidation of 2,3-*O*-isopropylidene-D-mannose, followed by H_2SO_4 deprotection.

[r] The starting (2*R*,4*R*)-2,3,4-trihydroxypentanedial was generated in situ by $PhI(OAc)_2$ oxidation of 1,2-*O*-isopropylidene-D-galactose, followed by H_2SO_4 deprotection.

[s] The starting (*meso*)-2,3,4-trihydroxylpentanedial was generated in situ by $PhI(OAc)_2$ oxidation of 1,2-*O*-isopropylidene-D-allose, followed by H_2SO_4 deprotection.

[t] The starting aldehyde was stored as the corresponding dimethyl acetal and deprotected right before being used.

[u] The starting aldehyde was generated in situ from L-arabinose.

[v] The starting aldehyde was generated in situ from D-arabinose.

[w] The starting aldehyde was generated in situ from D-lyxose.

[x] The starting aldehyde was generated in situ from L-xylose.

[y] The starting aldehyde was generated in situ from D-xylose.

[z] The starting aldehyde was generated in situ from the corresponding (*E*)-vinyl sulfone by dihydroxylation with $ADmix_\alpha$ or $ADmix_\beta$. The overall yield from the (*E*)-vinyl sulfone is given.

[aa] The starting aldehyde was generated in situ by reaction of the corresponding (*E*)-vinyl sulfone with DHQD-IND-OsO_4 and $MeSO_2NH_2$. The overall yield from the (*E*)-vinyl sulfone is given.

[bb] The starting aldehyde was generated in situ from D-galactose.

[cc] The starting (2*S*)-2-hydroxy-2-phenylethanal was generated in situ from (5*S*)-2,2-dimethyl-5-phenyl-1,3-dioxolan-4-ol.

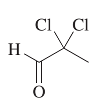
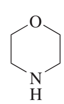
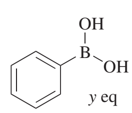
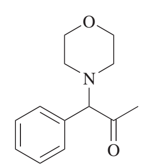
[dd] The starting (2*S*)-2-hydroxy-3-phenylpropanal was generated in situ from (5*S*)-2,2-dimethyl-5-phenylmethyl-1,3-dioxolan-4-ol.

[ee] The diastereomer ratio was determined by ^1H NMR spectroscopy.

[ff] The reaction was run with 4 Å molecular sieves.

[gg] The starting (2*R*)-2-hydroxy-3-phenylpropanal was generated in situ from (5*R*)-2,2-dimethyl-5-phenylmethyl-1,3-dioxolan-4-ol.

TABLE 4. α-AMINO KETONES FROM ALDEHYDES, AMINES, AND ORGANOBORON REAGENTS

Aldehyde	Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3					
	 *x* eq	 *y* eq	See table.		46

x	*y*		Solvent(s)	Temp	Time	Purity (%)	
1	1	—	toluene	rt	18 h	—	(0)[b]
1	1	—	toluene	reflux	18 h	93[a]	(16)[b]
3	1	—	toluene	reflux	18 h	94[a]	(39)[b]
1	1	MW	toluene	150°	33 min	97[a]	(21)[b]
3	1	MW	toluene	150°	33 min	94[a]	(32)[b]
3	2	—	toluene	rt	18 h	—	(0)[b]
3	2	—	toluene	reflux	18 h	79[a]	(50)[b]
3	3	—	toluene	reflux	18 h	78[a]	(33)[b]
3	2	—	toluene/H_2O (99:1)	reflux	18 h	78[a]	(22)[b]
3	1	—	CH_2Cl_2	reflux	18 h	—	(0)[b]
3	2	—	DMSO	110°	18 h	—	(0)[b]
3	2	—	DCE	reflux	18 h	94[a]	(46)[b]
3	2	—	toluene	70°	18 h	77[a]	(32)[b]
3	2	—	toluene/HFIP (9:1)	50°	18 h	45[a]	(10)[b]
3	2	pressure tube	toluene/HFIP (9:1)	110°	18 h	60[c]	(22)[c]

TABLE 4. α-AMINO KETONES FROM ALDEHYDES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

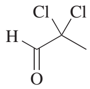
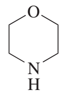
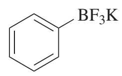
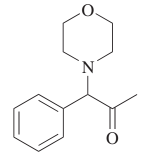
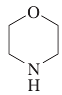
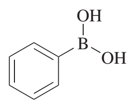
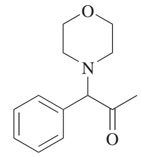
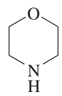
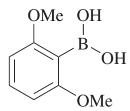
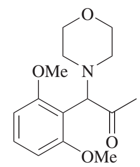
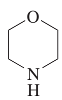
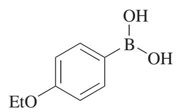
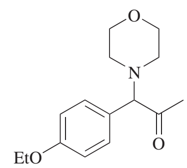
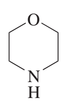
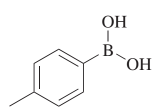
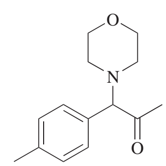
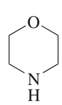
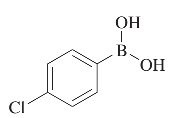
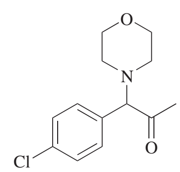
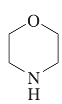
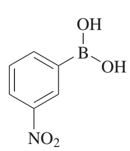
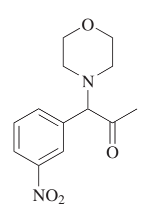
Aldehyde	Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 			BF_3•OEt_2, toluene, reflux, 18 h	 (2)[b] 5% pure [a]	46
			Et_3N, toluene, reflux, 18 h	 (13)[b] 40% pure [a]	46
			Toluene, reflux, 18 h	 (50)[b] 84% pure [a]	46
			Toluene, reflux, 18 h	 (63)[b] (23)[d] 91% pure [a]	46
			Toluene, reflux, 18 h	 (44)[b] (12)[d] 81% pure [a]	46
			Toluene, reflux, 18 h	 (18)[b] (2)[d] 46% pure [a]	46
			Toluene, reflux, 18 h	 (trace)	46

TABLE 4. α-AMINO KETONES FROM ALDEHYDES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

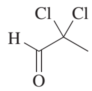
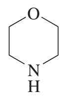
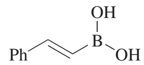
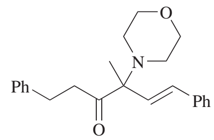
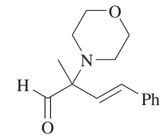
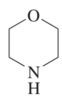
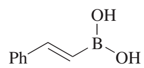
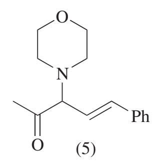
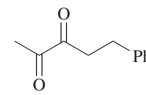
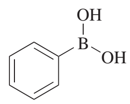
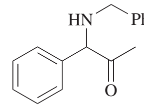
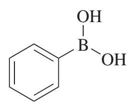
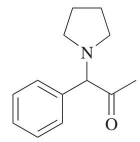
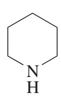
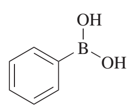
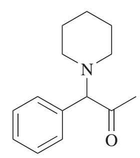
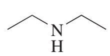
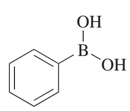
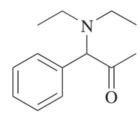
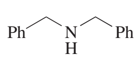
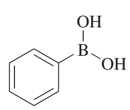
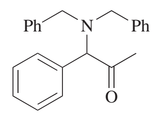
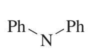
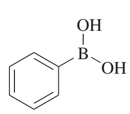
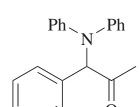
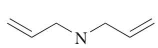
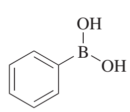
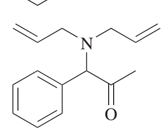
Aldehyde	Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3					
			Toluene, reflux, 18 h	 (21) +  (2)	46
			CH_2Cl_2 or $CHCl_3$, reflux, 18 h	 (5) +  (5)	46
			Toluene, reflux, 18 h	 (0)	46
			Toluene, reflux, 18 h	 (trace)	46
			Toluene, reflux, 18 h	 (trace)	46
			Toluene, reflux, 18 h	 (trace)	46
			Toluene, reflux, 18 h	 (trace)	46
			Toluene, reflux, 18 h	 (trace)	46
			Toluene, reflux, 18 h	 (trace)	46

TABLE 4. α-AMINO KETONES FROM ALDEHYDES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

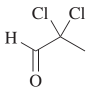
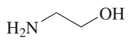
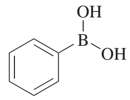
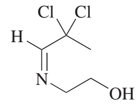
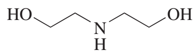
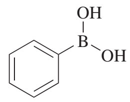
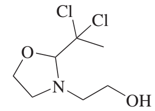
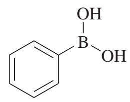
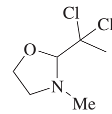
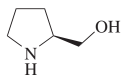
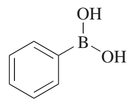
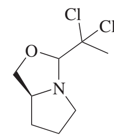
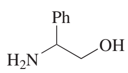
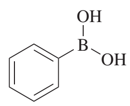
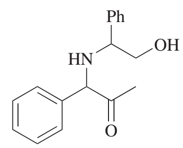
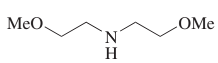
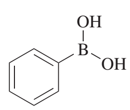
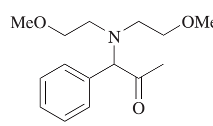
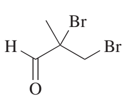
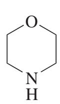
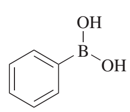
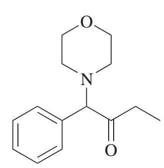
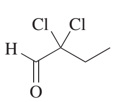
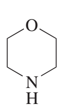
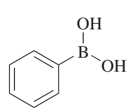
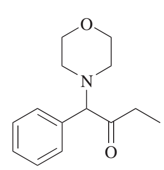
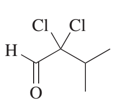
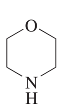
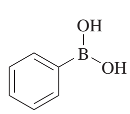
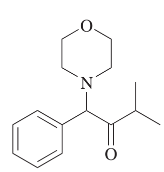
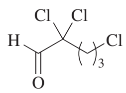
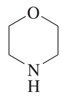
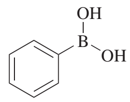
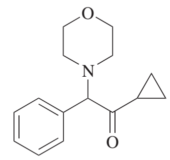
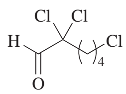
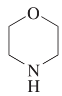
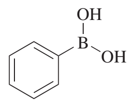
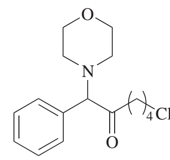
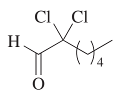
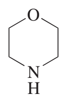
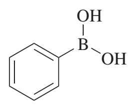
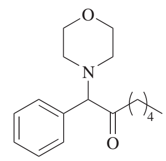
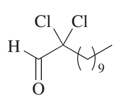
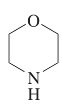
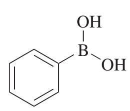
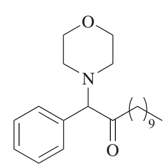
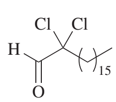
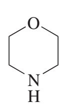
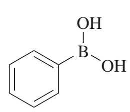
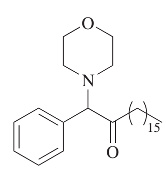
Aldehyde	Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3					
			Toluene, reflux, 18 h	 (11)	46
			Toluene, reflux, 18 h	 (11)	46
			Toluene, reflux, 18 h	 (43)	46
			Toluene, reflux, 18 h	 (71)	46
			DCE, reflux, 18 h	 (0)	46
			DCE, reflux, 18 h	 (0)	46
C_4					
			Toluene, reflux, 18 h	 (35)	46
			Toluene, reflux, 18 h	 (36)[b] (10)[d] 72% pure [a]	46
C_5					
			Toluene, reflux, 18 h	 (49)[b] (19)[d] 96% pure [a]	46

TABLE 4. α-AMINO KETONES FROM ALDEHYDES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Aldehyde	Amine	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5					
			Toluene, reflux, 18 h	 (20)	46
C_6					
			Toluene, reflux, 18 h	 (22)	46
C_7					
			Toluene, reflux, 18 h	 (54)[b] (24)[d] 90% pure [a]	46
C_{12}					
			Toluene, reflux, 18 h	 (1)[b] 25% pure [a]	46
C_{18}					
			Toluene, reflux, 18 h	 (0.3)[b] 8% pure [a]	46

[a] The purity was determined by GC–MS analysis of the crude mixture.

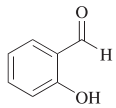
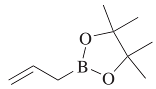
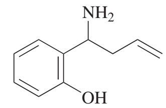
[b] The yield was calculated from the GC–MS analysis of the crude mixture.

[c] The purity and yield were determined by ^{1}H NMR analysis.

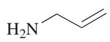
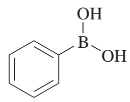
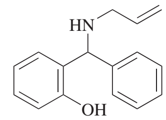
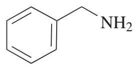
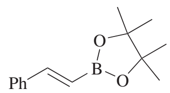
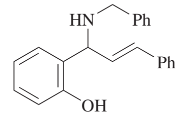
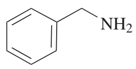
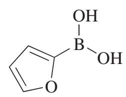
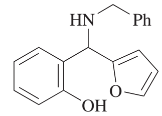
[d] The yield was determined after flash chromatography.

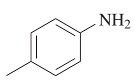
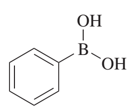
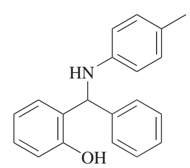
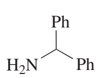
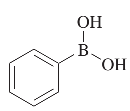
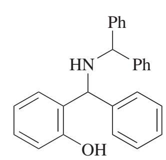
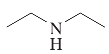
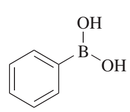
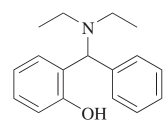
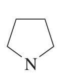
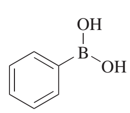
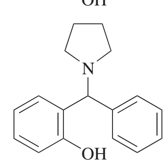
[e] This value is LC–MS area % purity as judged by Evaporative Light Scattering (ELS).

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7						
	NH_3		See table.			

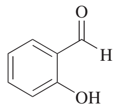
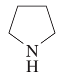
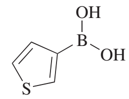
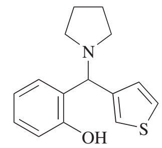
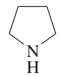
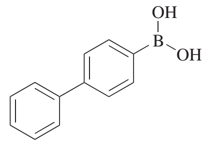
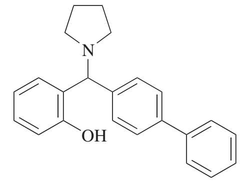
NH_3	Solvent	Additive	Temp	Time (h)		Refs.
liquid	EtOH	—	–10° then rt	3 then 1	(76)	28
25% aq	—	DBSA	rt	2	(75)	49

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
			MW, 120°, 2 h		(44)	51
			Solvent, rt		Solvent MeOH, Time (h) 72, (0); Solvent HFIP, Time (h) 4, (0)	21
			MeOH, rt, 24–36 h		(32)	14

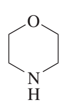
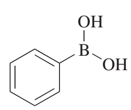
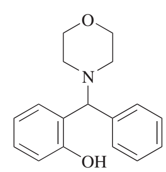
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
			CH_2Cl_2, MW, 120°, 10 min		0% conv Product: imine	50
			CH_2Cl_2, MW, 120°, 10 min		0% conv Product: imine	50
			80°, 2 h		(45)	112
			See table.			

Solvent	Temp (°)	Time (h)		Refs.
H_2O	80	24	(78)	16
—	80	2	(83)	112

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

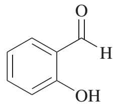
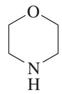
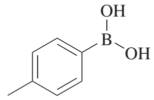
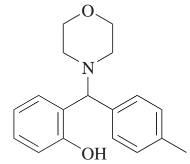
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 			H_2O, 80°, 24 h	 (94)	16
			Solvent, rt		52

Solvent	Time (h)	
$BminBF_4$	3.5	(82)
MeOH	12	(60)

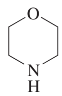
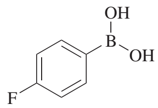
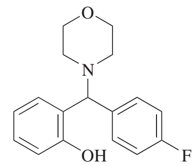
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			See table.		

	Solvent	Temp (°)	Time	Conv (%)		Refs.
MW	—	90	2 h	87	—	51
MW	—	120	2 h	99	(78)	51
MW	—	150	45 min	99	—	51
—	—	120	2 h	84	—	51
MW	CH_2Cl_2	120	10 min	77	(76)	50
—	dioxane	90	16 h	—	(93)	47
—	H_2O	80	24 h	—	(75)	16
—	H_2O	80	4.5 h	—	(54)	16
—	EtOH	80	24 h	—	(63)	16
—	DME	80	5 h	—	(69)	16
—	DMF	80	5 h	—	(41)	16
—	toluene	80	5 h	—	(75)	16
—	DCE	80	5 h	—	(77)	16
—	—	rt	6 h	—	(13)	112
—	—	40	6 h	—	(57)	112
—	—	60	6 h	—	(82)	112
—	—	80	6 h	—	(97)	112
—	—	100	6 h	—	(82)	112
—	—	80	30 min	—	(82)	112
—	—	80	1 h	—	(89)	112
—	—	80	2 h	—	(92)	112
—	—	80	3 h	—	(92)	112

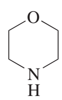
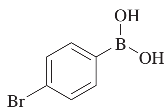
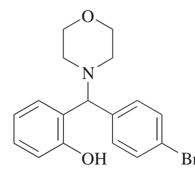
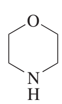
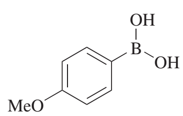
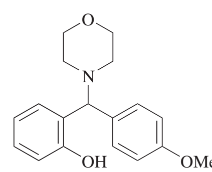
TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 			See table.		

	Solvent	Temp (°)	Time (h)		Refs.
MW	—	120	2	(87)	51
—	H_2O	80	4.5	(85)	16
—	—	80	2	(95)	112

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			See table.		

	Solvent	Temp (°)	Time	Conv (%)		Refs.
MW	CH_2Cl_2	120	10 min	57	(75)	50
—	H_2O	80	4.5 h	—	(75)	16
—	—	80	2 h	—	(89)	112

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			80°, 2 h	 (91)	112
			See table.		

Solvent	Temp (°)	Time (h)		Refs.
H_2O	80	4.5	(81)	16
—	80	2	(94)	112

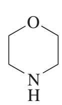
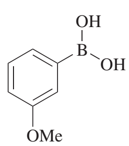
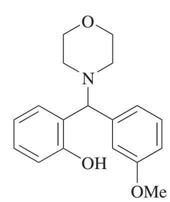
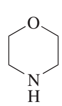
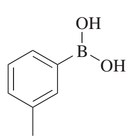
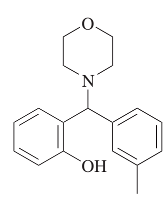
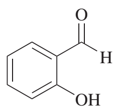
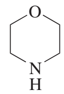
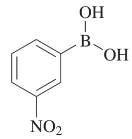
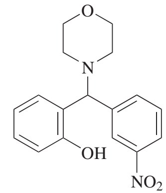
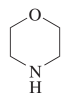
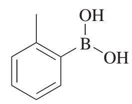
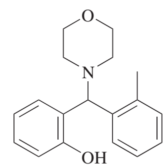
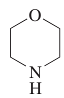
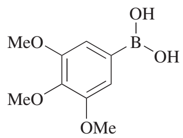
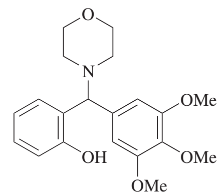
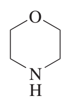
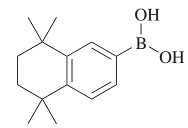
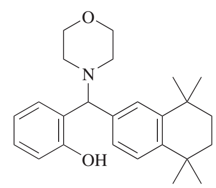
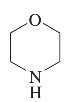
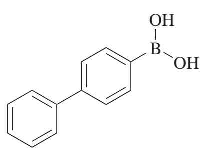
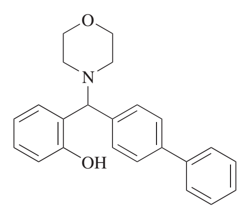
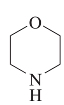
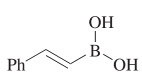
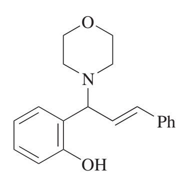
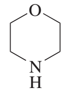
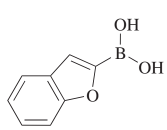
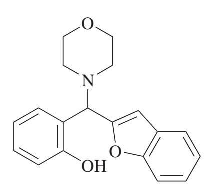
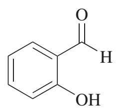
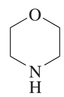
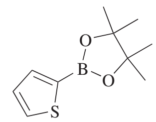
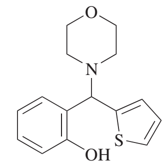
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			CH_2Cl_2, MW, 120°, 10 min	 (62), 57% conv	50
			MW, 120°, 2 h	 (78)	51

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

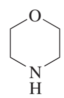
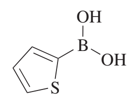
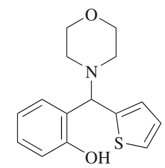
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7 			MW, 120°, 2 h		(87)	51
			MW, 120°, 2 h		(72)	51
			MW, 120°, 2 h		(92)	51
			MW, 120°, 2 h		(96)	51
			$BmimBF_4$, rt, 3 h		(80)	52
			EtOH, rt, 24–36 h		(88)	14
			See table.			

	Solvent	Temp (°)	Time	Conv (%)		Refs.
MW	CH_2Cl_2	120	10 min	92	(23)	50
MW	—	120	2 h	—	(95)	51

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7					
			See table.		21

	Solvent	Temp	Time	
MW, 300W	MeOH	120°	10 min	(28)
—	HFIP	rt	4 h	(65)

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			See table.		

Solvent	Temp (°)	Time (h)		Refs.
$BmimBF_4$	80	5	(75)	52
—	80	2	(96)	112

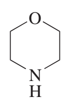
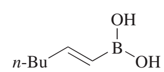
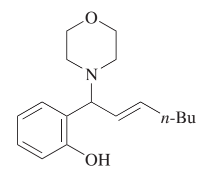
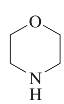
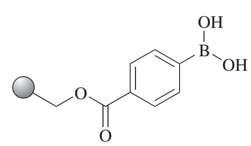
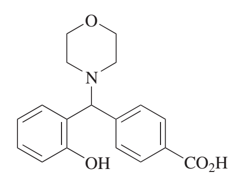
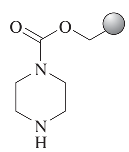
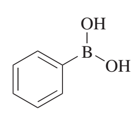
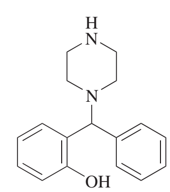
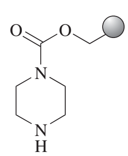
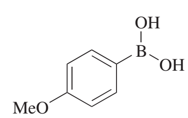
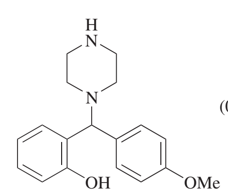
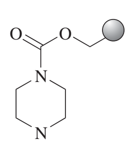
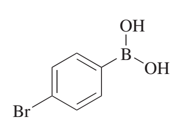
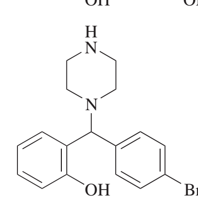
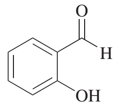
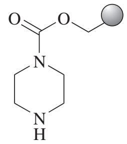
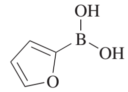
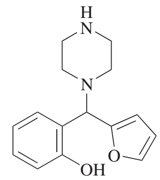
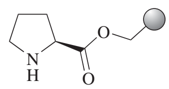
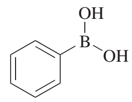
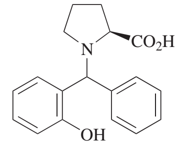
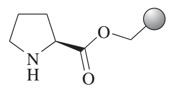
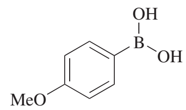
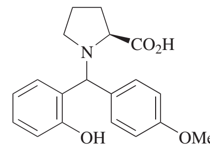
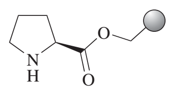
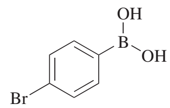
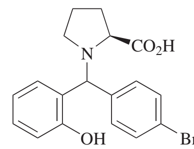
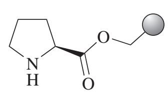
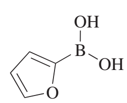
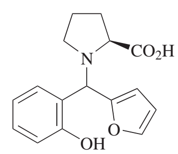
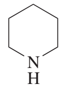
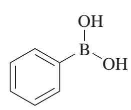
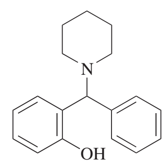
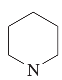
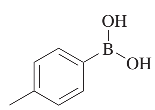
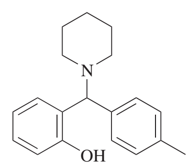
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			Dioxane, 90°, 12 h	 (80)	47
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 (29)[a] >95% pure	13
			1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 (63)[b] 85% pure	13
			1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 (0)	13
			1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h	 (63)[b] 88% pure	13

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7 			1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(0)	13
			1. DMF/DCE, (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(82)[c] dr 94:6 >95% pure	13
			1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(41)[c] dr 87:13 84% pure	13
			1. DMF/DCE (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(81)[c] dr 97.5:2.5 95% pure	13

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
			1. DMF/DCE, (2:3), 50°, 48 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(0)	13
			See table.			

	Solvent	Temp (°)	Time (h)		Refs.
MW	—	120	2	(85)	51
—	—	80	2	(81)	112

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
			See table.			

	Solvent	Temp (°)	Time (h)		Refs.
MW	—	120	2	(82)	51
—	H_2O	80	24	(96)	16

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

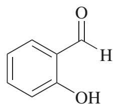
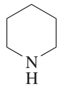
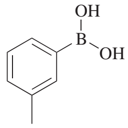
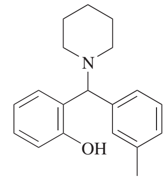
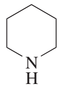
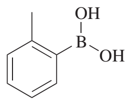
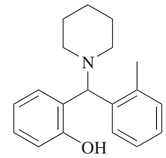
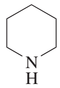
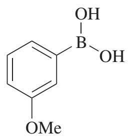
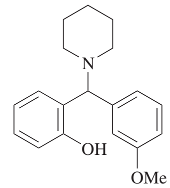
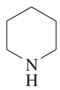
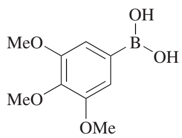
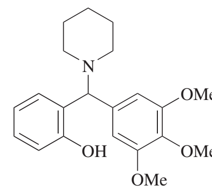
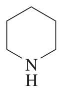
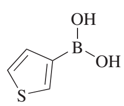
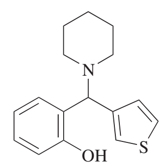
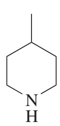
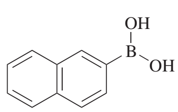
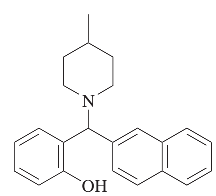
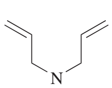
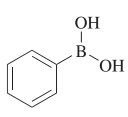
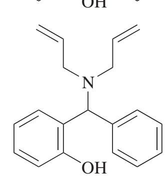
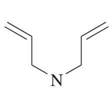
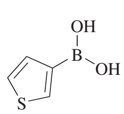
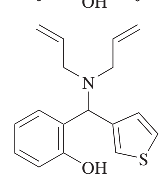
Aldehyde	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	 	MW, 120°, 2 h	 (82)	51
	 	MW, 120°, 2 h	 (87)	51
	 	MW, 120°, 2 h	 (80)	51
	 	MW, 120°, 2 h	 (89)	51
	 	H_2O, 80°, 24 h	 (91)	16
	 	$BmimBF_4$, 80°, 4 h	 (79)	52
	 	H_2O, 80°, 24 h	 (82)	16
	 	H_2O, 80°, 24 h	 (96)	16

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

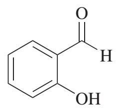
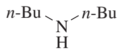
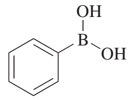
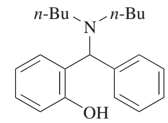
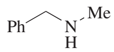
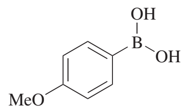
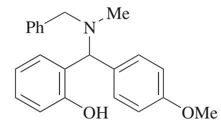
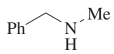
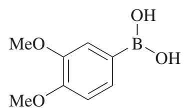
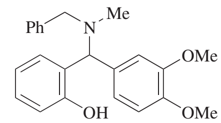
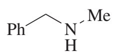
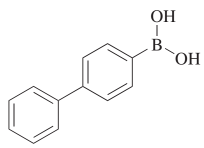
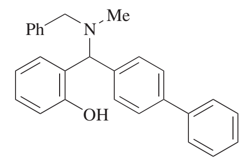
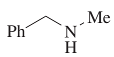
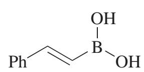
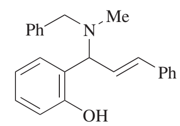
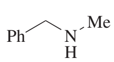
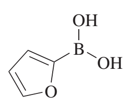
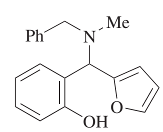
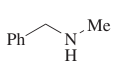
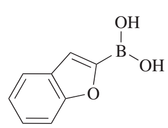
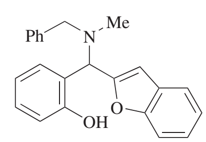
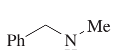
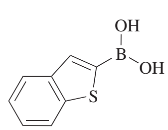
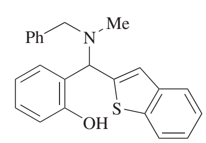
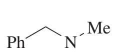
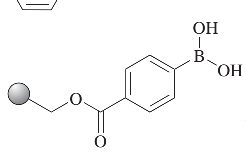
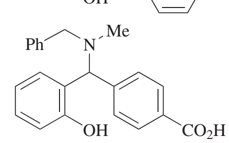
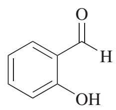
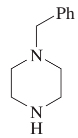
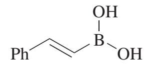
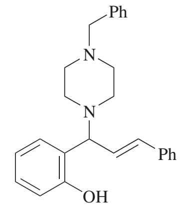
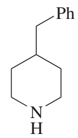
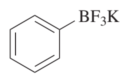
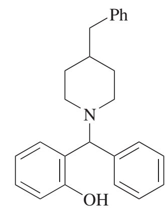
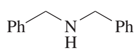
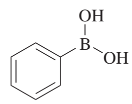
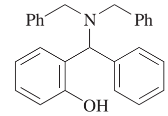
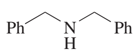
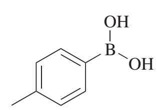
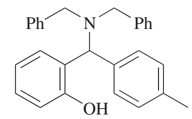
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7 			80°, 2 h		(51)	112
			H_2O, 80°, 24 h		(98)	16
			EtOH, rt, 24–36 h		(70)	14
			$BmimBF_4$, rt, 4 h		(80)	52
			EtOH, rt, 24–36 h		(81)	14
			See table.			
				Solvent / Temp / Time (h)		
				EtOH / rt / 24–36	(79)	14
				H_2O / 80° / 24	(79)	16
			EtOH, rt, 24–36 h		(52)	14
			EtOH, rt, 24–36 h		(50)	14
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(20)[a] >95% pure	13

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7 			EtOH, rt, 24–36 h		(58)	14
			1. Aldehyde, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 1 min; then 90°, 1 h		(75)	48
			See table.			

	Solvent	Temp (°)	Time		Refs.
MW	CH_2Cl_2	120	10 min	(50)	50
MW	—	120	2 h	(85)	51
—	—	80	2 h	(80)	112

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
			See table.			

	Solvent	Temp (°)	Time (h)		Refs.
MW	—	120	2	(92)	51
—	H_2O	80	24	(99)	16

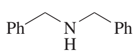
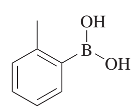
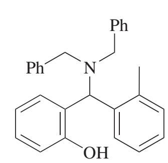
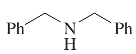
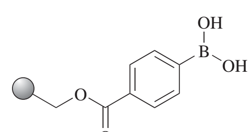
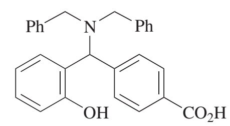
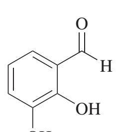
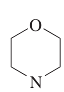
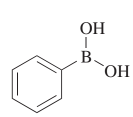
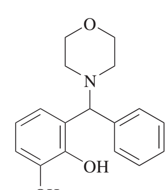
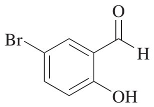
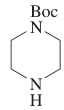
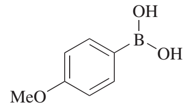
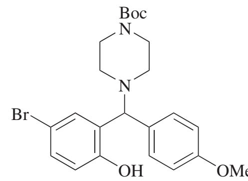
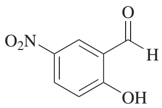
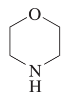
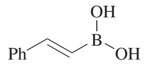
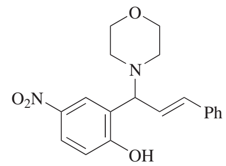
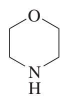
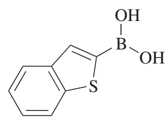
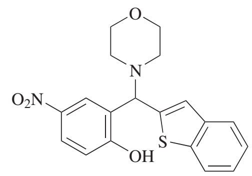
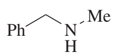
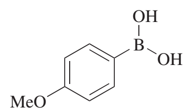
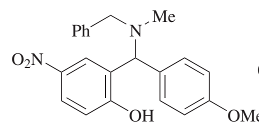
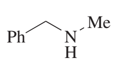
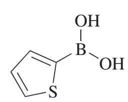
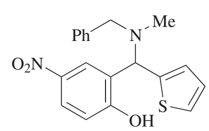
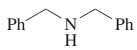
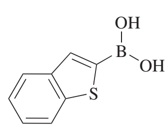
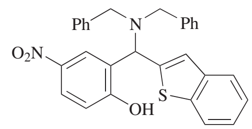
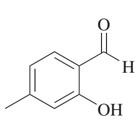
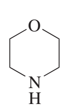
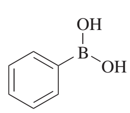
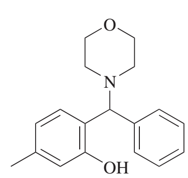
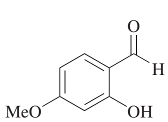
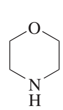
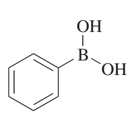
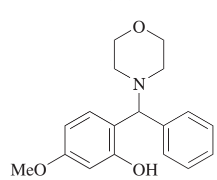
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
			MW, 120°, 2 h		(90)	51
			1. DMF/DCE (2:3), 50°, 20 h 2. TFA/CH_2Cl_2 (1:1), rt, 0.5 h		(20)[a] >95% pure	13
			Dioxane, 90°, 16 h		(88)	47

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7					
			EtOH, rt, 24–36 h	 (63)	14
			EtOH, rt, 24–36 h	 (40)	14
			EtOH, rt, 24–36 h	 (62)	14
			EtOH, rt, 24–36 h	 (65)	14
			EtOH, rt, 24–36 h	 (66)	14
			EtOH, rt, 24–36 h	 (70)	14
C_8					
			See table.		
			See table.		

First C_8 entry:

Solvent	Temp (°)	Time (h)		Refs.
H_2O	80	24	(70)	16
—	80	2	(86)	112

Second C_8 entry:

Solvent	Temp (°)	Time (h)		Refs.
H_2O	80	24	(72)	16
—	80	2	(89)	112

TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

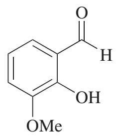
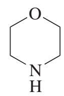
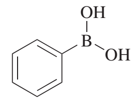
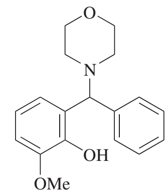
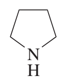
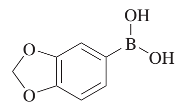
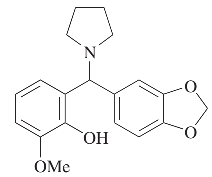
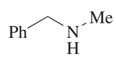
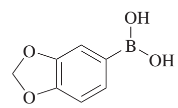
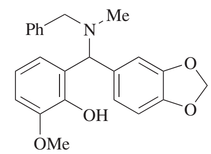
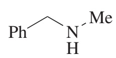
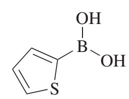
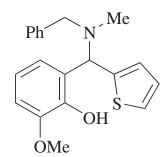
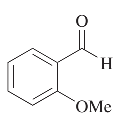
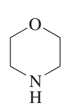
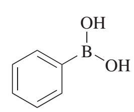
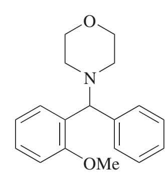
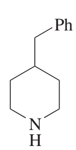
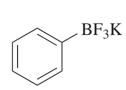
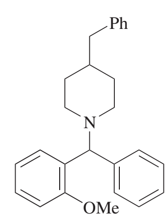
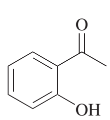
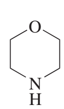
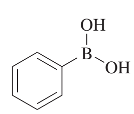
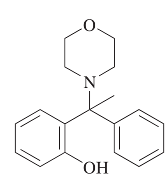
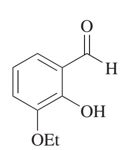
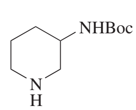
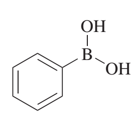
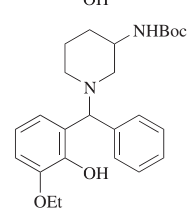
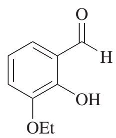
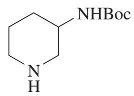
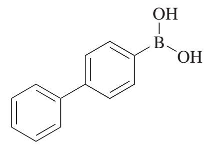
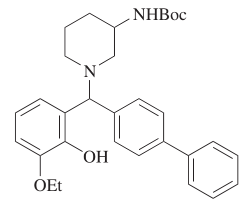
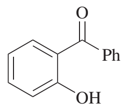
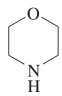
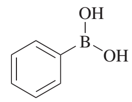
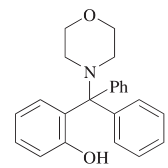
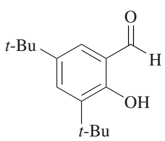
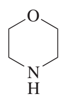
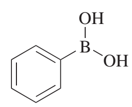
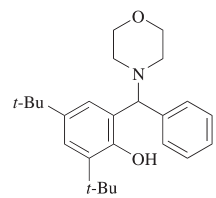
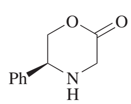
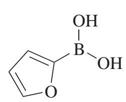
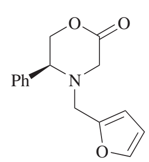
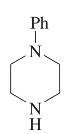
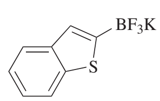
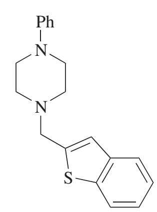
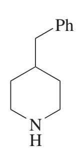
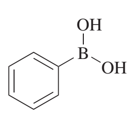
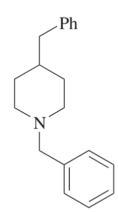
Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_8 			Dioxane, 90°, 16 h		(90)	47
			$BmimBF_4$, rt, 3 h		(80)	52
			$BmimBF_4$, rt, 3 h		(70)	52
			$BmimBF_4$, 80°, 4 h		(76)	52
			Dioxane, 90°, 16 h		(0)	47
			1. Aldehyde, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 1 min; then 90°, 1 h		(0)	48
			Dioxane, 90°, 16 h		(0)	47
C_9 			$BmimBF_4$, rt, 3 h		(70)	52

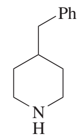
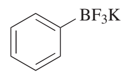
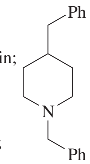
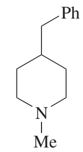
TABLE 5. 2-HYDROXYBENZYLAMINES FROM SALICYLALDEHYDE AND DERIVATIVES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Aldehyde	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_9						
			BmimBF$_4$, rt, 5 h		(85)	52
C_{13}						
			Dioxane, 90°, 16 h		(0)	47
C_{15}						
			80°, 2 h		(82)	112

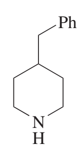
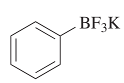
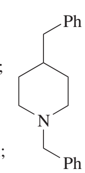
[a] The yield was determined by ^{1}H NMR spectroscopy using DMSO-d_5 as the internal standard, based on the theoretical loading of Wang aldehyde resin (2.45 mmol/g).
[b] The yield was determined by ^{1}H NMR spectroscopy using DMSO-d_5 as the internal standard, based on the theoretical loading of Wang aldehyde resin (1.04 mmol/g).
[c] The yield was determined by ^{1}H NMR spectroscopy using DMSO-d_5 as the internal standard, based on the theoretical loading of the Fmoc-Proline Wang resin (0.84 mmol/g).

TABLE 6. AMINOMETHYLARENES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_1						
$(CHO)_n$			THF, reflux, 1–2 h		(69)	8
			1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 1 min; then 90°, 1 h		(95)	48
			1. Dioxane, 90°, 10 min; then rt 2. $PhB(OH)_2$, 90°, 24 h		(10–20)	48

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1					
$(CHO)_n$			1. $(CHO)_n$, amine, solvent, temp, 10 min; then rt 2. Organoboron, BF_3•OEt_2, rt, 5 min; then heating	 I +  II	48

Solvent	Temp (°)	I	II
dioxane	rt	"no reaction"	—
dioxane	60	"very sluggish"	—
dioxane	>80	(60)	—
DCE	>80	(70)	—
toluene	>80	(75)	—
THF	>80	—, (<60)[a]	—
DME	>80	—, (<60)[a]	—
HOAc	>80	—, (<60)[a]	—
MeCN	>80	—	"major"
DMF	>80	—	"major"
DMSO	>80	—	"major"

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			1. $(CHO)_n$, amine, toluene, 90°, 10 min; then rt 2. Organoboron, Lewis acid, rt, 5 min; then 90°, 5 h		48

Lewis acid	
—	(0)
BF_3•OEt_2 (10 mol %)	(59)
BF_3•OEt_2 (20–25 mol %)	(75)
BF_3•OEt_2 (100 mol %)	(78)
BF_3•OEt_2 (200 mol %)	(0)
TiF_4	(90)
$Zn(OTf)_2$	(—)[b]
$Cu(OTf)_2$	(—)[b]
$Sn(OTf)_2$	(—)[b]
$La(OTf)_3$	(—)[b]
$Y(OTf)_3$	(—)[b]
$Sc(OTf)_3$	(—)[b]
TMSCl	(—)[b]
$MgBr_2$•OEt_2	(—)[b]
n-Bu_2BOTf	(—)[c]
AgOTf	(—)[c]
TMSOTf	(—)[c]
$SnCl_4$	(—)[d]
$AlMe_3$	(—)[d]

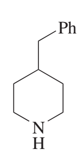
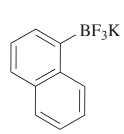
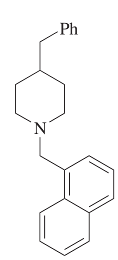
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (86)	48

TABLE 6. AMINOMETHYLARENES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

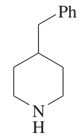
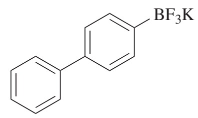
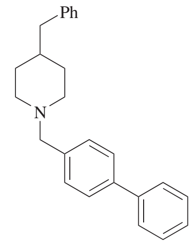
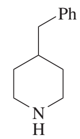
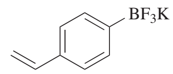
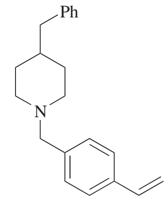
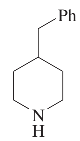
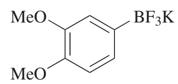
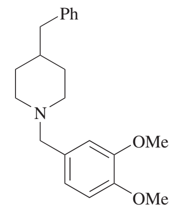
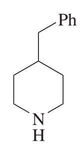
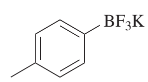
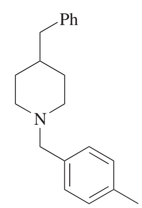
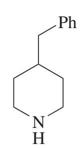
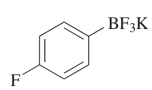
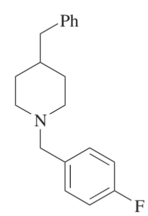
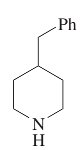
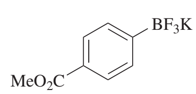
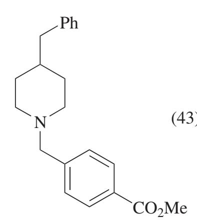
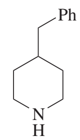
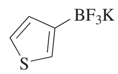
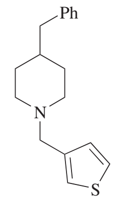
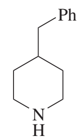
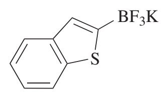
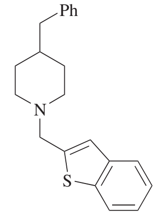
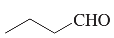
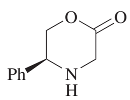
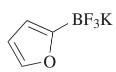
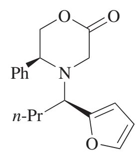
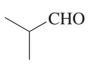
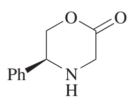
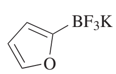
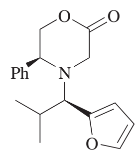
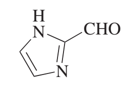
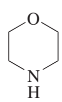
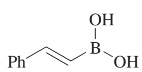
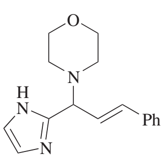
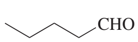
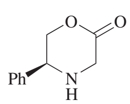
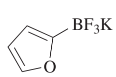
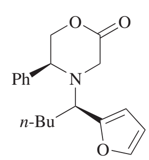
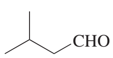
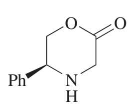
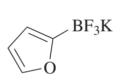
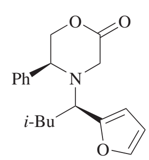
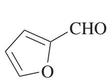
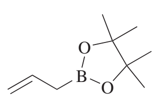
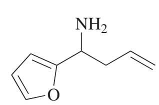
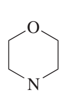
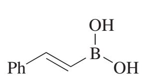
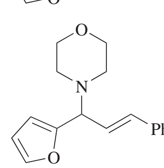
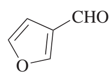
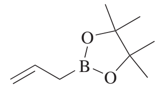
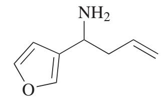
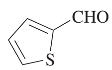
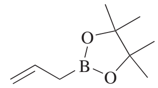
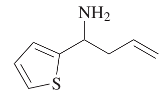
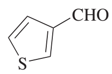
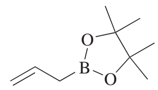
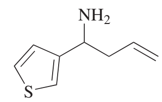
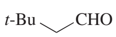
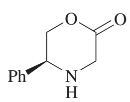
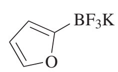
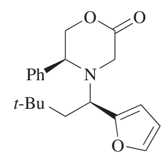
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
$(CHO)_n$	 	1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (81)	48
	 	1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (75)	48
	 	1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (85)	48
	 	1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (67)	48
	 	1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (79)	48
	 	1. $(CHO)_n$, amine, HOAc, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (43)	48

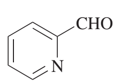
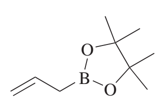
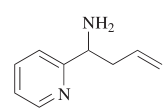
TABLE 6. AMINOMETHYLARENES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_1						
$(CHO)_n$			1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h		(82)	48
			1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h		(98)	48
C_4						
			THF, reflux, 3 h		(59) dr 96.5:3.5	8, 113
			THF, reflux, 3 h		(7) dr >97.5:2.5	8, 113
			DMF/CH_2Cl_2 (4:6), 50°, 48 h		(—)	53
C_5						
			THF, reflux, 3 h		(69) dr 95:5	8, 113
			THF, reflux, 3 h		(71) dr 96:4	8
	NH_3 (25% aq)		DBSA (10 mol %), rt, 2 h		(53)	49
			DMF/CH_2Cl_2 (4:6), 50°, 48 h		(—)	53

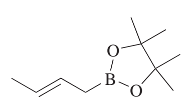
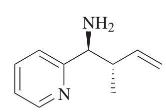
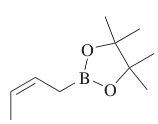
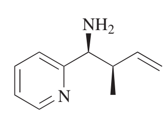
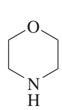
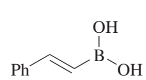
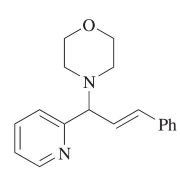
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_5						
	NH_3 (25% aq)		DBSA (10 mol %), rt, 2 h		(93)	49
	NH_3		See table.			

NH_3	Solvent	Additive	Temp	Time (h)		Refs.
liquid	EtOH	—	–10°; then rt	5; then 1	(77)	28
25% aq	—	DBSA (10 mol %)	rt	6	(60)	49

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
	NH_3 (25% aq)		DBSA (10 mol %), rt, 2 h		(95)	49
C_6						
			THF, reflux, 3 h		(75) dr 96:4 (75) dr 93:7	8 113

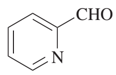
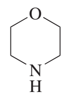
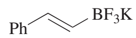
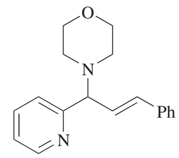
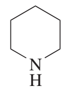
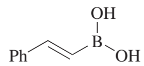
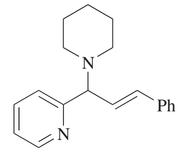
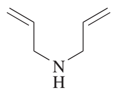
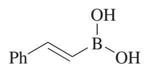
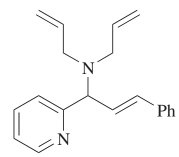
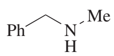
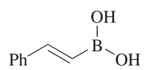
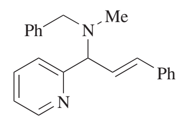
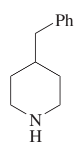
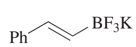
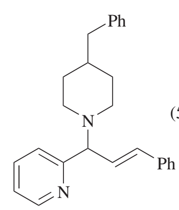
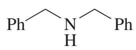
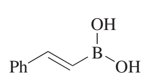
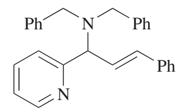
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
	NH_3		See table.			

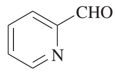
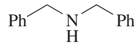
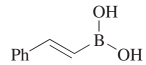
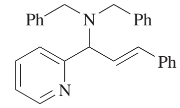
NH_3	Solvent	Additive	Temp	Time (h)		Refs.
liquid	EtOH	—	–10°; then rt	5; then 1	(85)	28
25% aq	—	DBSA (10 mol %)	rt	6	(88)	49

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
	NH_3 (25% aq)		DBSA (10 mol %), rt, 2 h	 major (*rac*)	(90) dr 95:5	49
	NH_3 (25% aq)		DBSA (10 mol %), rt, 2 h	 major (*rac*)	(87) dr 95:5	49
			See table.			

Solvent	Temp	Time (h)		Refs.
MeCN	reflux	15	(95)	54
DMF/CH_2Cl_2 (4:6)	50°	48	(10)	53

TABLE 6. AMINOMETHYLARENES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_6						
			TMSCl, THF, rt, 24 h		(54)	53
			MeCN, reflux, 15 h		(75)	54
			MeCN, reflux, 12 h		(72)	54
			MeCN, reflux, 15 h		(77)	54
			1. Aldehyde, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 1 min; then 90°, 1 h		(58)	48
			Solvent, rt, 15 h		Solvent / Conv (%) CH_2Cl_2 55 DCE 46 MeCN 73 HFIP 58 MeOH <10 toluene <10 THF <2 Et_2O <2 DMF <10 H_2O <10 $BdmimBF_4$ <2	54

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6					
 *x* M	 *x* M	 *x* M	MeCN, temp		54

x	Temp	Time (h)	Conv (%)	
0.1	rt	15	73	—
0.2	rt	15	73	—
0.5	rt	15	59	—
0.2	50°	15	84	—
0.2	reflux	15	>98	(96)
0.2	reflux	3	>98	(96)

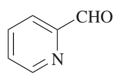
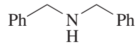
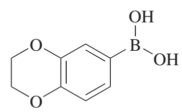
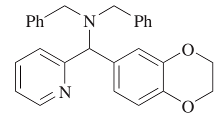
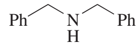
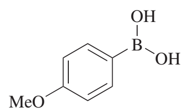
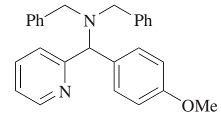
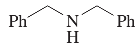
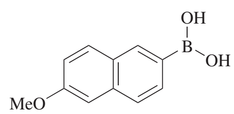
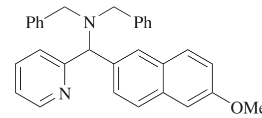
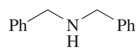
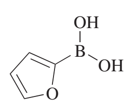
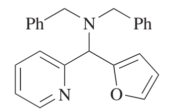
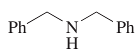
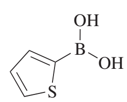
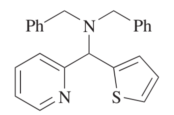
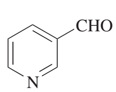
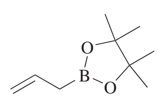
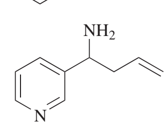
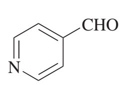
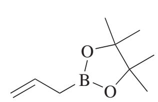
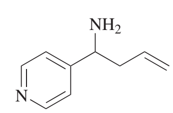
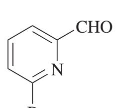
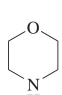
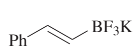
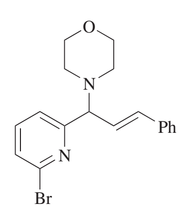
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			MeCN, reflux, 15 h	 (90)	54
			MeCN, reflux, 15 h	 (70)	54
		 *x* eq	MeCN, reflux, 15 h	 *x* 1.0 (27) 1.5 (46)	54
			MeCN, reflux, 15 h	 (80)	54
		 *x* eq	MeCN, reflux, 15 h	 *x* 1.0 (32) 1.5 (78)	54
	NH_3 (25% aq)		DBSA (10 mol %), rt, 2 h	 (85)	49
	NH_3 (25% aq)		DBSA (10 mol %), rt, 2 h	 (83)	49
			TMSCl, THF, rt, 24 h	 (28)	53

TABLE 6. AMINOMETHYLARENES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

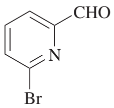
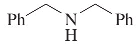
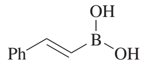
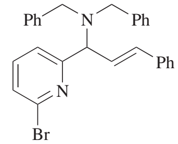
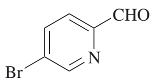
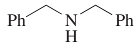
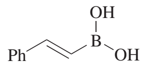
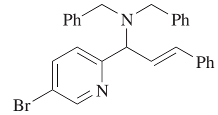
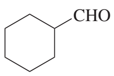
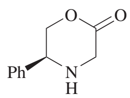
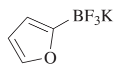
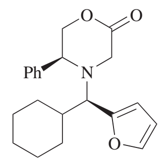
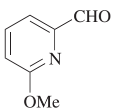
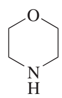
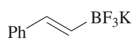
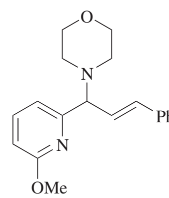
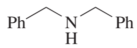
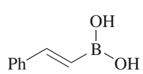
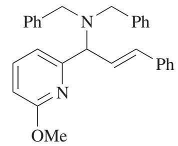
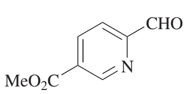
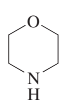
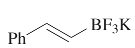
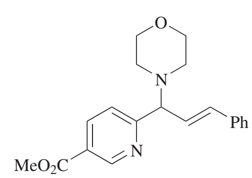
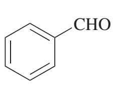
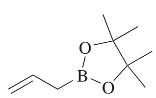
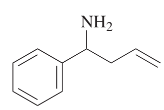
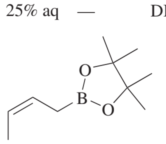
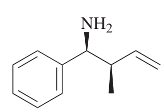
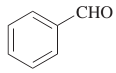
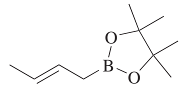
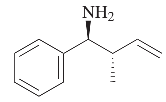
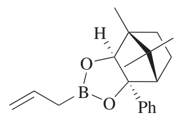
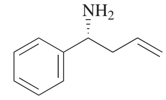
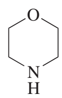
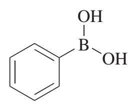
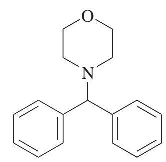
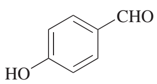
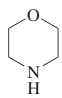
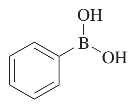
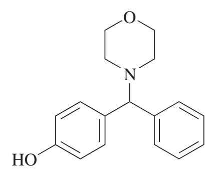
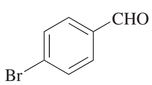
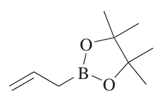
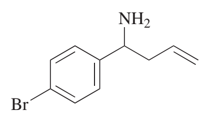
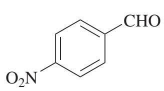
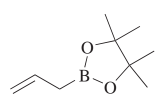
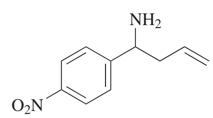
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_6						
		 *x* eq	MeCN, reflux, 15 h		*x*: 1.0 (11); 1.5 (23)	54
			MeCN, reflux, 15 h		(91)	54
C_7						
			THF, reflux, 3 h		(6) dr >97.5:2.5	8, 113
			TMSCl, THF, rt, 24 h		(40)	53
		 *x* eq	MeCN, reflux, 15 h		*x*: 1.0 (16); 1.5 (31)	54
			TMSCl, THF, rt, 24 h		(31)	53
	NH_3		See table.			
		NH_3 | Solvent | Additive	Temp	Time (h)		
		liquid | EtOH | —	–10°; then rt	5; then 1	(84)	28
		liquid | EtOH | —	rt	2.5	(80)	28
		25% aq | — | DBSA (10 mol %)	rt	6	(61)	49
	NH_3		1. Boronate, NH_3, EtOH, –78°; then rt, 30 min 2. Aldehyde, rt, 2 h	 major (*rac*)	(85) dr >99:1	28

TABLE 6. AMINOMETHYLARENES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	NH_3 	1. Boronate, NH_3, EtOH, –78°; then rt, 30 min 2. Aldehyde, rt, 2 h	 (79) dr 93:7 major (*rac*)	28
	NH_3 	1. Aldehyde, NH_3, CH_2Cl_2, –30°, 30 min 2. Boronate, –30°, 4 h; then rt, 1 h	 (74) er 67.0:33.0	28
	 	Dioxane, 90°, 16 h	 (0)	47
	 	Dioxane, 90°, 16 h	 (0)	47
	NH_3 	1. Aldehyde, NH_3, EtOH, –10°, 2 h 2. Boronate, –10°, 3 h; then rt, 1 h	 (92)	28
	NH_3 	See table.		

NH_3	Solvent	Additive	Temp	Time (h)		Refs.
liquid	EtOH	—	–10°; then rt	5; then 1	(96)	28
25% aq	—	DBSA (10 mol %)	rt	6	(60)	49

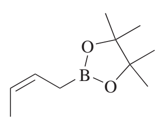
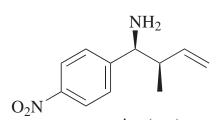
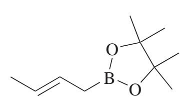
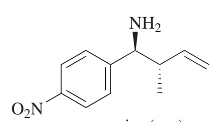
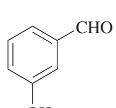
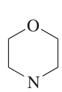
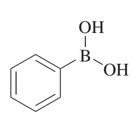
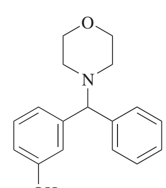
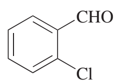
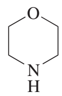
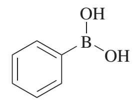
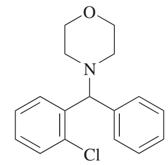
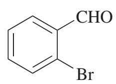
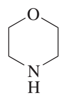
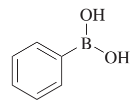
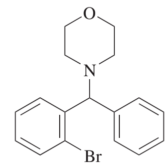
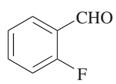
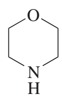
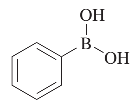
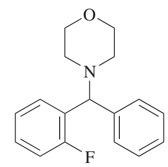
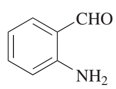
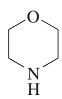
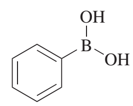
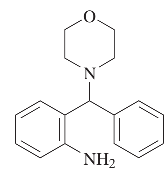
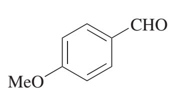
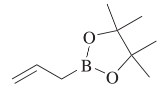
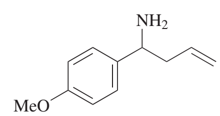
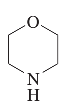
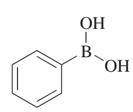
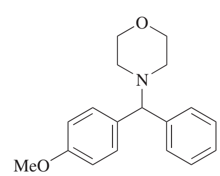
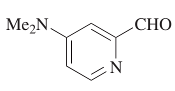
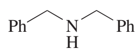
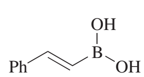
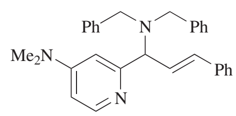
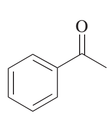
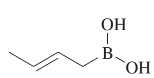
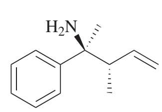
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3 	1. Boronate, NH_3, EtOH, –78°; then rt, 30 min 2. Aldehyde, rt, 2 h	 (90) dr >99:1 major (*rac*)	28
	NH_3 	1. Boronate, NH_3, EtOH, –78°; then rt, 30 min 2. Aldehyde, rt, 2 h	 (92) dr 92:8 major (*rac*)	28
	 	Dioxane, 90°, 16 h	 (0)	47

TABLE 6. AMINOMETHYLARENES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_7						
			Dioxane, 90°, 16 h		(0)	47
			Dioxane, 90°, 16 h		(0)	47
			Dioxane, 90°, 16 h		(0)	47
			Dioxane, 90°, 16 h		(0)	47
C_8						
	NH_3		See table.			

NH_3	Solvent	Additive	Temp	Time (h)		Refs.
liquid	EtOH	—	–10°; then rt	5; then 1	(91)	28
25% aq	—	DBSA (10 mol %)	rt	6	(60)	49

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
			Dioxane, 90°, 16 h		(0)	47
			MeCN, reflux, 15 h		(35)	54
	NH_3		MeOH, rt, 24 h	 major (*rac*)	(50) dr 97:3	29

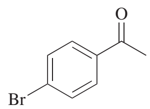
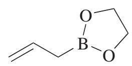
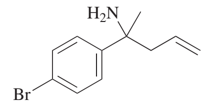
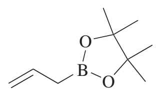
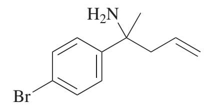
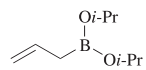
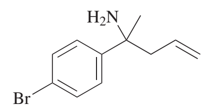
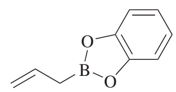
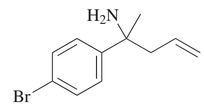
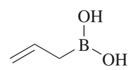
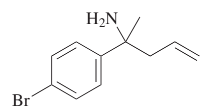
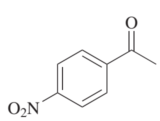
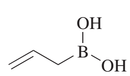
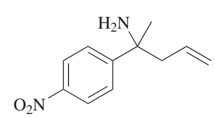
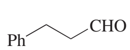
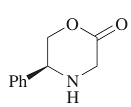
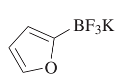
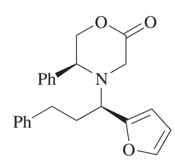
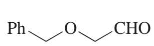
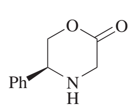
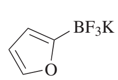
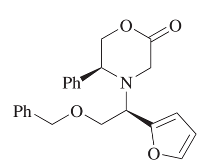
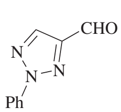
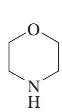
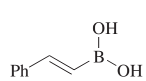
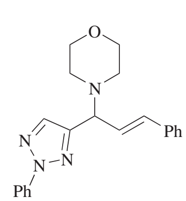
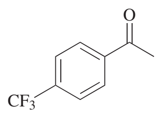
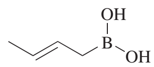
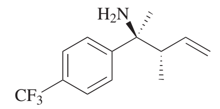
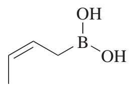
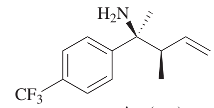
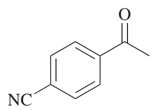
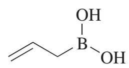
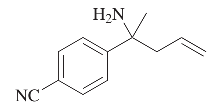
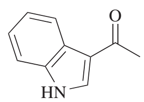
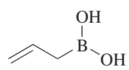
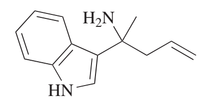
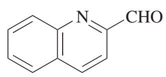
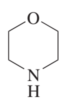
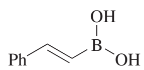
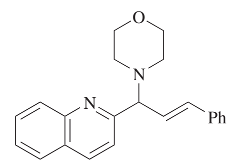
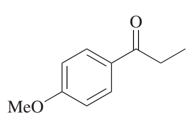
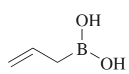
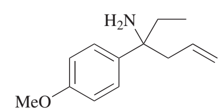
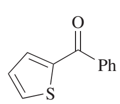
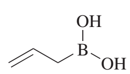
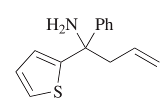
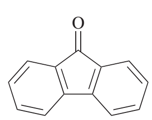
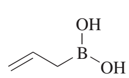
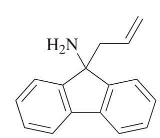
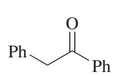
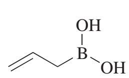
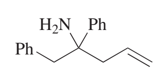
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_8					
	NH_3		MeOH, rt, 16 h	 (35)	29
	NH_3		MeOH, rt, 16 h	 (29)	29
	NH_3		MeOH, rt, 16 h	 (43)	29
	NH_3		MeOH, rt, 16 h	 (70)	29
	NH_3		MeOH, rt, 16 h	 (79)	29
	NH_3		MeOH, rt, 16 h	 (87)	29
C_9					
			THF, reflux, 3 h	 (66) dr 94.5:5.5	8, 113
			THF, reflux, 3 h	 (64) dr 93:7	8, 113
			DMF/CH_2Cl_2 (4:6), 50°, 48 h	 (—)	53

TABLE 6. AMINOMETHYLARENES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)		Refs.
C_9						
	NH_3		MeOH, rt, 24 h	 major (*rac*)	(80) dr 97:3	29
	NH_3		MeOH, rt, 24 h	 major (*rac*)	(73) dr 96:4	29
	NH_3		MeOH, rt, 16 h		(80)	29
C_{10}						
	NH_3		MeOH, rt, 16 h		(80)	29
			DMF/CH_2Cl_2 (4:6), 50°, 48 h		(—)	53
	NH_3		MeOH, rt, 16 h		(72)	29
C_{11}						
	NH_3		MeOH, rt, 16 h		(75)	29
C_{13}						
	NH_3		MeOH, rt, 16 h		(78)	29
C_{14}						
	NH_3		MeOH, rt, 16 h		(78)	29

[a] The yield was not reported but was described to be "lower" than the three yields given for **I**.

[b] The yield was described as "moderate to excellent".

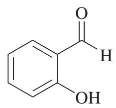
[c] A mixture of products was obtained.

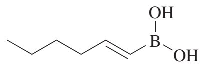
[d] Degradation of the product mixture occurred.

TABLE 7A. HETEROCYCLES: 2*H*-CHROMENES FROM SALICYLADEHYDE AND DERIVATIVES, ORGANOBORON REAGENTS, AND AMINES

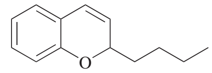
Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.

C_7

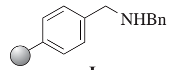




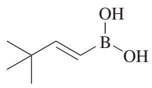
See table.



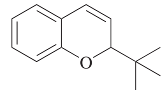
Amine	Solvent	Temp (°)	Time (h)		Refs.
Bn_2NH (20 mol %)	$BmimBF_4$	80	3	(94)	58
Bn_2NH (5 mol %)	dioxane	90	12	(92)	47
I (40 mol %)	dioxane	90	24	(99)	47



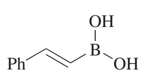
I



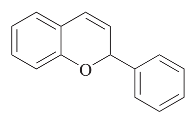
Amine **I**[a] (40 mol %), dioxane, 90°, 24 h



(96) 47

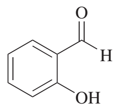
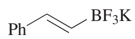
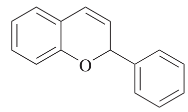
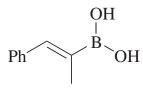
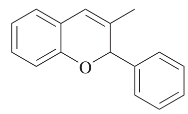
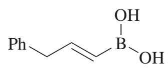
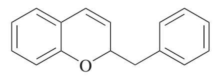
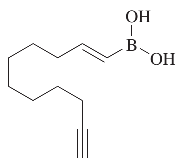
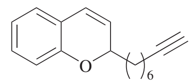
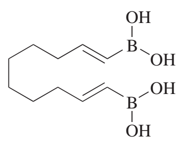
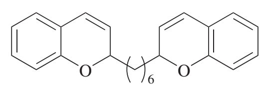


See table.

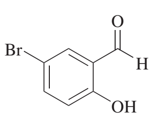
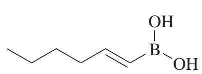
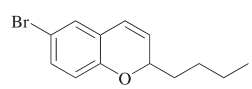
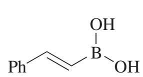
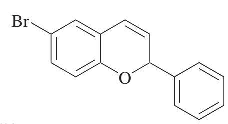


Amine	Base	Solvent	Temp (°)	Time (h)		Refs.
Bn_2NH (20 mol %)	—	$BmimBF_4$	80	3	(92)	58
Bn_2NH (20 mol %)	—	$EmimBF_4$	80	3	(91)	58
Bn_2NH (20 mol %)	—	BmimBr	80	3	(89)	58
Bn_2NH (20 mol %)	—	$BmimPF_6$	80	3	(7)	58
Me_2NH•HCl (1.2 eq)	NaOH (2 eq)	H_2O	80	24	(79)	56, 16
Bn_2NH (1.2 eq)	—	H_2O	80	24	(58)	56, 16
Et_2NH (1.2 eq)	—	H_2O	80	24	(92)	56, 16
Et_2NH (20 mol %)	—	H_2O	80	24	(49)	56, 16
Et_2NH (40 mol %)	—	H_2O	80	24	(71)	56
Et_2NH (1.2 eq)	—	H_2O	80	5	(66)	56
Et_2NH (1.2 eq)	—	H_2O	50	5	(58)	56
Et_2NH (1.2 eq)	—	DCE	80	5	(62)	56
Et_2NH (1.2 eq)	—	dioxane	80	5	(60)	56
I[a] (40 mol %)	—	dioxane	90	24	(96)	47

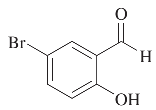
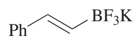
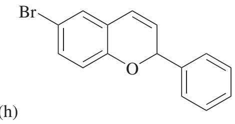
TABLE 7A. HETEROCYCLES: 2*H*-CHROMENES FROM SALICYLADEHYDE AND DERIVATIVES, ORGANOBORON REAGENTS, AND AMINES (*Continued*)

Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (51)	57
		Amine **I**[a] (40 mol %), dioxane, 90°, 24 h	 (75)	47
		Et_2NH (*x* eq), H_2O, 80°, 24 h	 *x* 1.2 (78); 0.4 (75)	56, 16; 56
		Amine **I**[a] (40 mol %), dioxane, 90°, 24 h	 (95)	47
		See table.		

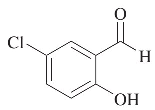
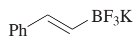
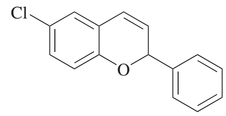
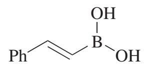
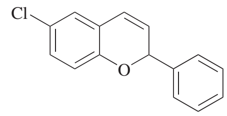
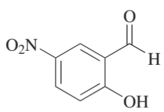
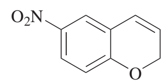
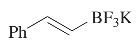
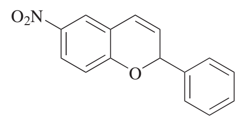
Amine	Solvent	Temp (°)	Time (h)		Refs.
I[a] (40 mol %)	dioxane	90	24	(91)	47
Bn_2NH (20 mol %)	$BmimBF_4$	80	3	(88)	58

Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		Amine **I**[a] (40 mol %), dioxane, 90°, 24 h	 (90)	47
		See table.		55

Amine	Solvent	Temp (°)	Time	
Bn_2NH (1 eq)	H_2O	80	3 h	(82)
Et_3N (1 eq)	EtOH	70	24 h	(53)
Et_3N (2 eq)	EtOH	70	24 h	(61)
Et_3N (10 mol %)	EtOH	70	24 h	traces
Et_3N (1 eq)	H_2O	70	48 h	(38)
i-Pr_2NEt (1 eq)	EtOH	70	24 h	(31)
i-Pr_2NEt (1 eq)	EtOH	70	7 d	(37)
DABCO (1 eq)	EtOH	70	7 d	(14)
TMP	EtOH	70	24 h	traces
$PhNMe_2$	EtOH	70	24 h	(0)
pyridine	EtOH	70	24 h	(0)
Bu_4NOH	EtOH	70	24 h	(0)

Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		See table.		

Amine	Solvent	Temp (°)	Time (h)		Refs.
Bn_2NH (1 eq)	H_2O	80	3	(82)	55
Bn_2NH (20 mol %)	DMF	80	17	(71)	57

Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (89)	57
		Bn_2NH (20 mol %), $BmimBF_4$, 80°, 3 h	 (88)	58
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (65)	57
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (90)	57

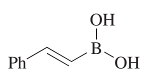
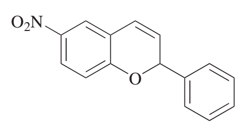
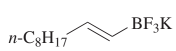
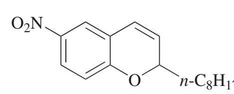
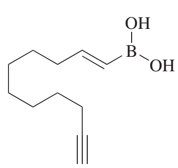
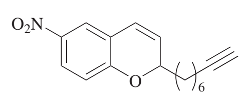
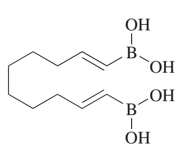
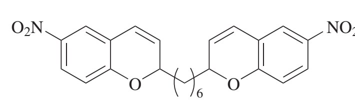
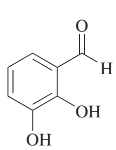
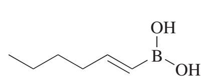
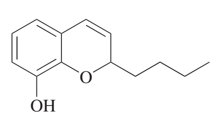
Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
		Bn_2NH (20 mol %), $BmimBF_4$, 80°, 3 h	 (91)	58
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (85)	57
		Bn_2NH (20 mol %), $BmimBF_4$, 80°, 3 h	 (91)	58
		Bn_2NH (20 mol %), $BmimBF_4$, 80°, 3 h	 (87)	58
		Amine **I**[a] (40 mol %), dioxane, 90°, 24 h	 (88)	47

TABLE 7A. HETEROCYCLES: 2*H*-CHROMENES FROM SALICYLADEHYDE AND DERIVATIVES, ORGANOBORON REAGENTS, AND AMINES (*Continued*)

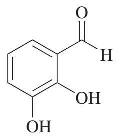
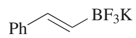
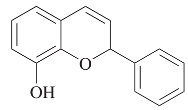
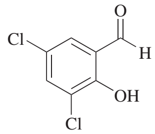
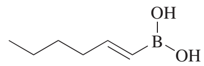
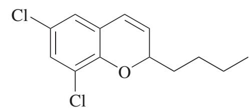
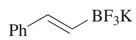
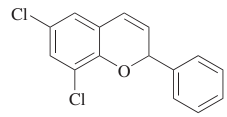
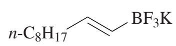
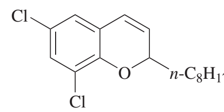
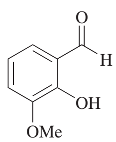
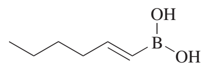
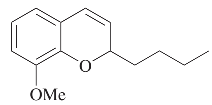
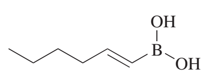
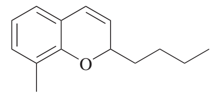
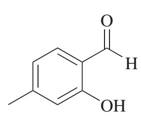
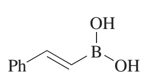
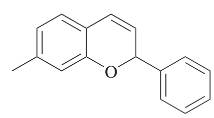
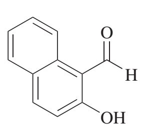
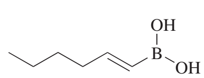
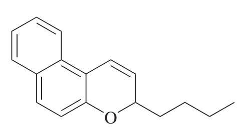
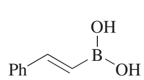
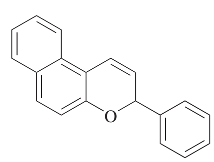
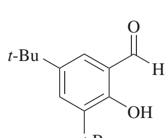
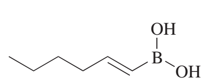
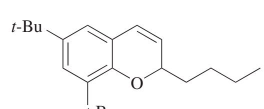
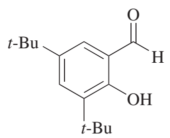
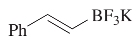
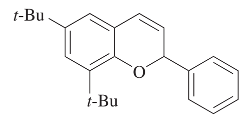
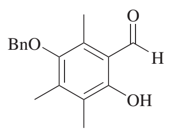
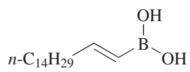
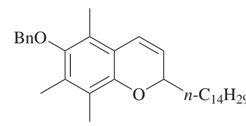
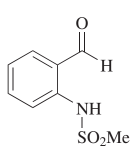
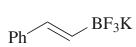
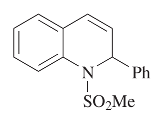
Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (54)	57
		Amine **I**[a] (40 mol %), dioxane, 90°, 24 h	 (91)	47
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (83)	57
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (87)	57
C_8				
		Amine **I**[a] (40 mol %), dioxane, 90°, 24 h	 (91)	47
		Bn_2NH (20 mol %), $BmimBF_4$, 80°, 3 h	 (87)	58
		Et_2NH (*x* eq), H_2O, 80°, 24 h	 *x* 1.2 (92) 0.4 (74)	 56, 16 56
C_{11}				
		Amine **I**[a] (40 mol %), dioxane, 90°, 24 h	 (93)	47
		Bn_2NH (20 mol %), $BmimBF_4$, 80°, 3 h	 (90)	58
C_{15}				
		Amine **I**[a] (40 mol %), dioxane, 90°, 24 h	 (85)	47

TABLE 7A. HETEROCYCLES: 2*H*-CHROMENES FROM SALICYLADEHYDE AND DERIVATIVES, ORGANOBORON REAGENTS, AND AMINES (*Continued*)

Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}				
		Bn_2NH (20 mol %), DMF, 80°, 17 h	 (78)	57
C_{17}				
		Bn_2NH (1 eq), *n*-BuOH, 110°, 24 h	 (57)	55

[a] Please refer to the first entry of this Table (7A) for the structure of amine **I**.

TABLE 7B. HETEROCYCLES: 1,2-DIHYDROQUINOLINES FROM 2-SULFAMIDOBENZALDEHYDE AND DERIVATIVES, ALKENYL TRIFLUOROBORATES, AND AMINES

Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		R_3N, Lewis acid, toluene, 80°, 18 h		55

Amine	Lewis Acid		
Et_3N (2 eq)	TMSCl (1 eq)	MeCN	(21)
Et_3N (excess)	TMSCl (2 eq)	—	(32)
Et_3N (5 eq)	TMSCl (5 eq)	—	(0)
Et_3N (2 eq)	TMSCl (2 eq)	—	(59)
i-Pr_2NEt (2 eq)	TMSCl (2 eq)	—	(31)
Et_3N (2 eq)	TMSCl (2 eq)	4 Å MS	(27)
Et_3N (2 eq)	TMSOTf (2 eq)	—	(35)
Et_3N (2 eq)	TBSCl (2 eq)	—	(48)
Et_3N (2 eq)	$BF_3{\bullet}OEt_2$ (2 eq)	—	(44)
Et_3N (2 eq)	BCl_3 (2 eq)	—	mixture
Et_3N (2 eq)	$AlCl_3$ (2 eq)	—	traces
Et_3N (2 eq)	$ZnBr_2$ (2 eq)	—	(0)
Et_3N (2 eq)	$FeCl_3$ (2 eq)	—	(0)
Et_3N (2 eq)	$TiCl_4$ (2 eq)	—	(0)
Et_3N (2 eq)	Ti(O*i*-Pr)$_4$ (2 eq)	—	(0)

TABLE 7B. HETEROCYCLES: 1,2-DIHYDROQUINOLINES FROM 2-SULFAMIDOBENZALDEHYDE AND DERIVATIVES, ALKENYL TRIFLUOROBORATES, AND AMINES (*Continued*)

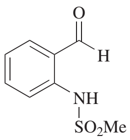
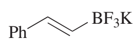
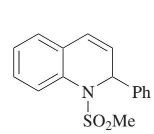
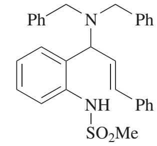
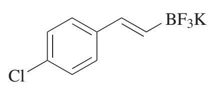
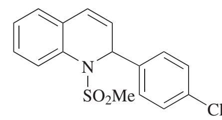
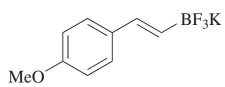
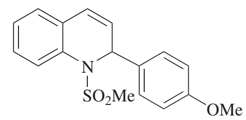
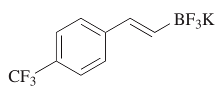
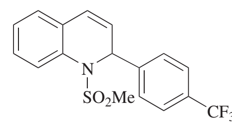
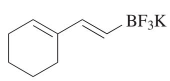
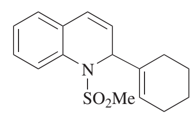
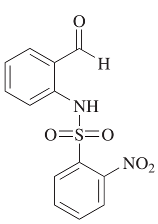
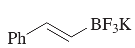
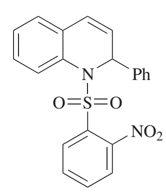
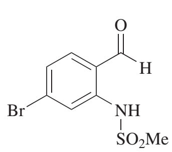
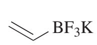
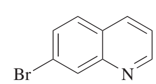
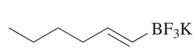
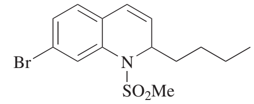
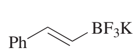
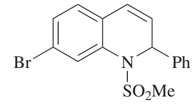
Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Bn_2NH, BF_3•OEt_2 (2 eq), toluene, 80°, 18 h	 (30) +  (26)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (48)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (26)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (33)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (60)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (36)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (18)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (32)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (59)	55

TABLE 7B. HETEROCYCLES: 1,2-DIHYDROQUINOLINES FROM 2-SULFAMIDOBENZALDEHYDE AND DERIVATIVES, ALKENYL TRIFLUOROBORATES, AND AMINES (*Continued*)

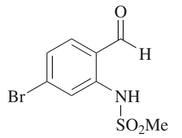
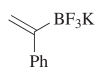
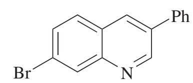
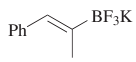
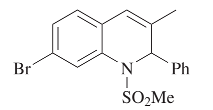
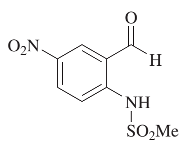
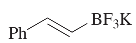
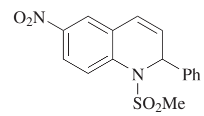
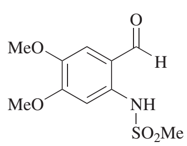
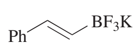
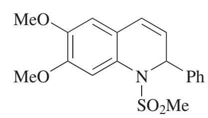
Aldehyde	Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (0)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (0)	55
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (53)	55
C_9				
		Et_3N (2 eq), TMSCl (2 eq), toluene, 80°, 18 h	 (46)	55

TABLE 7C. HETEROCYCLES: 2-HYDROXY AND 2-AMINOMORPHOLINES FROM GLYOXAL AND DERIVATIVES, BORONIC ACIDS, AND 1,2-AMINO ALCOHOLS

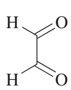
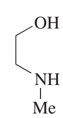
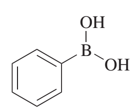
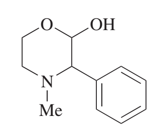
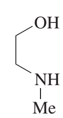
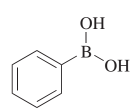
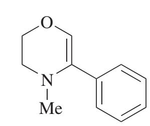
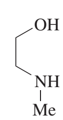
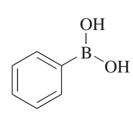
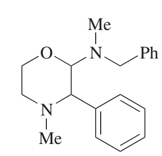
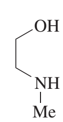
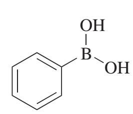
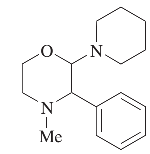
Aldehyde	1,2-Amino Alcohol	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
			EtOH, rt, 12 h	 (62) dr 95:5	59
			MW, 110°, 30 min	 (85)	60
			$PhCH_2NHMe$, MW, 110°, 15 min	 (76) dr 100:0	60
			Piperidine, MW, 110°, 15 min	 (77) dr 100:0	60

TABLE 7C. HETEROCYCLES: 2-HYDROXY AND 2-AMINOMORPHOLINES FROM GLYOXAL AND DERIVATIVES, BORONIC ACIDS, AND 1,2-AMINO ALCOHOLS (*Continued*)

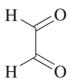
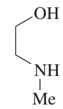
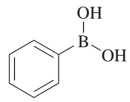
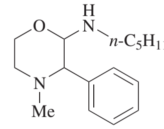
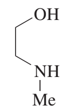
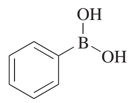
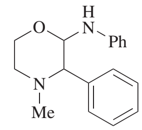
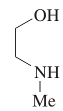
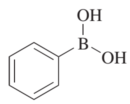
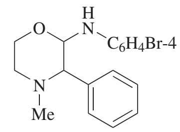
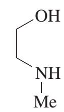
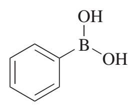
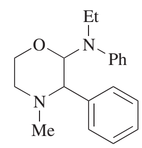
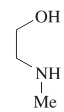
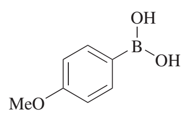
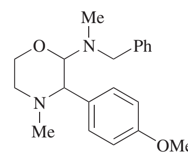
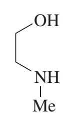
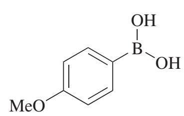
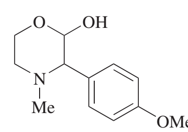
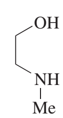
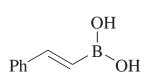
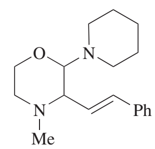
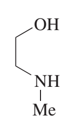
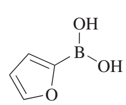
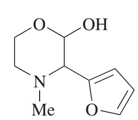
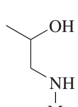
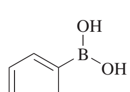
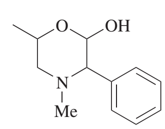
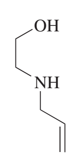
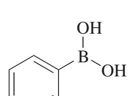
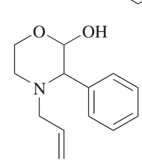
Aldehyde	1,2-Amino Alcohol	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
			n-$C_5H_{11}NH_2$ MW, 110°, 15 min	 (55) dr 93:7	60
			$PhNH_2$, MW, 110°, 15 min	 (50) dr 100:0	60
			4-$BrC_6H_4NH_2$ MW, 110°, 15 min	 (63) dr 100:0	60
			PhNHEt, MW, 110°, 15 min	 (62) dr 100:0	60
			$PhCH_2NHMe$, MW, 110°, 15 min	 (76) dr 100:0	60
			EtOH, rt, 12 h	 (80) dr 90:10	59
			Piperidine, MW, 110°, 15 min	 (43) dr 100:0	60
			EtOH, rt, 12 h	 (65) dr 70:30	59
			EtOH, rt, 24 h	 (65)[a]	61
			EtOH, rt, 12 h	 (75) dr 75:25	59

TABLE 7C. HETEROCYCLES: 2-HYDROXY AND 2-AMINOMORPHOLINES FROM GLYOXAL AND DERIVATIVES, BORONIC ACIDS, AND 1,2-AMINO ALCOHOLS (*Continued*)

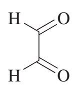
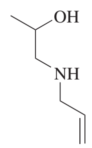
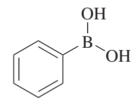
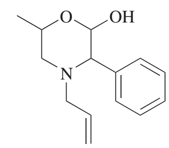
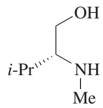
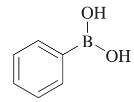
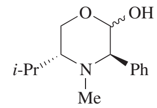
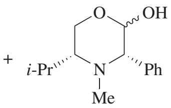
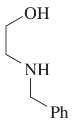
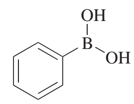
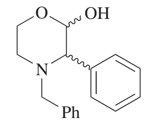
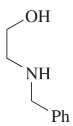
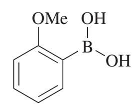
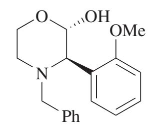
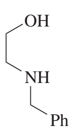
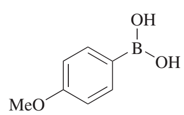
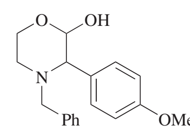
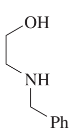
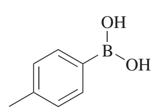
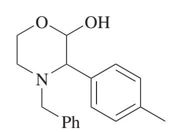
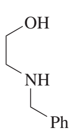
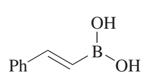
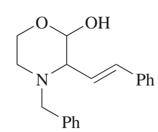
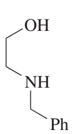
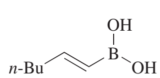
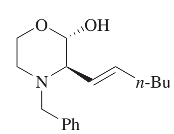
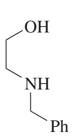
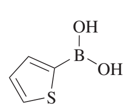
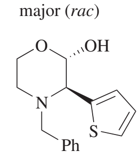
Aldehyde	1,2-Amino Alcohol	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
			EtOH, rt, 12 h	 (43)[a]	59
			EtOH, rt, 12 h	 I +  II **I** + **II** (74), **I**/**II** = 91:9	59
			Solvent, rt		
			Solvent / Time (h)	/ dr / Major	
			EtOH / 12	(70) 85:15 *trans*	59
			EtOH / 24	(70) 87:13 *trans*	61
			H_2O / 24	(97) 77:23 —	56
			EtOH, rt, 12 h	 major (*rac*) (50) dr 80:20	59, 61
			H_2O, rt, 24 h	 (94) dr 81:19	56
			H_2O, rt, 48 h	 (93) dr 83:17	56
			H_2O, rt, 48 h	 (89) dr 53:47	56
			EtOH, rt	 major (*rac*) Time (h) / dr 12 (67) 60:40 24 (66) 55:45	59 61
			EtOH, rt	 major (*rac*) Time (h) / dr 12 (65) 75:25 24 (56) 75:25	59 61

TABLE 7C. HETEROCYCLES: 2-HYDROXY AND 2-AMINOMORPHOLINES FROM GLYOXAL AND DERIVATIVES, BORONIC ACIDS, AND 1,2-AMINO ALCOHOLS (*Continued*)

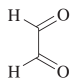
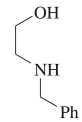
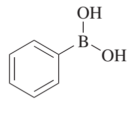
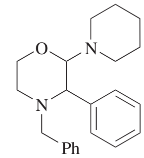
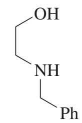
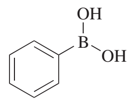
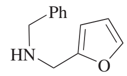
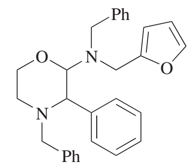
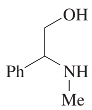
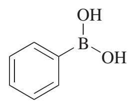
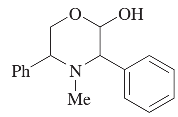
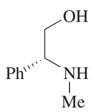
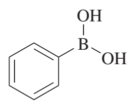
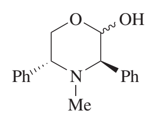
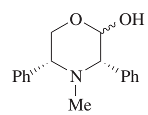
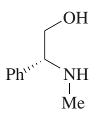
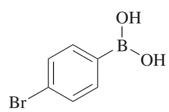
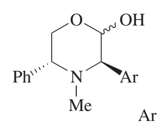
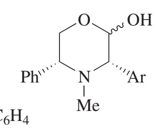
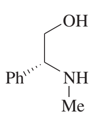
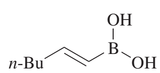
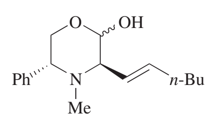
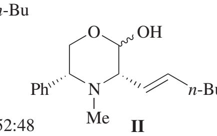
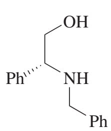
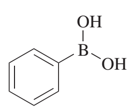
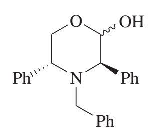
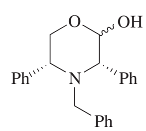
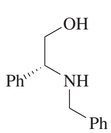
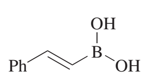
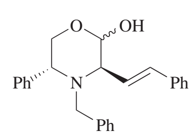
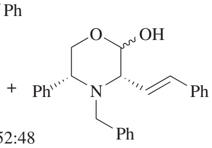
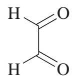
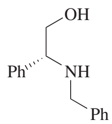
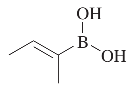
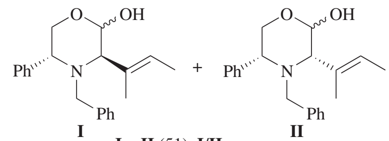
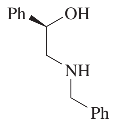
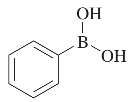
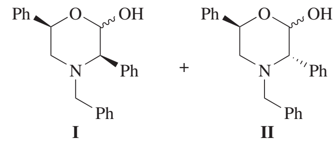
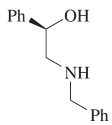
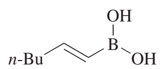
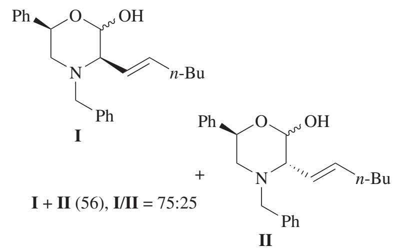
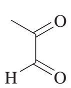
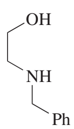
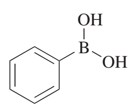
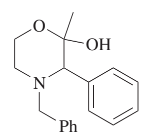
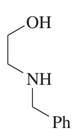
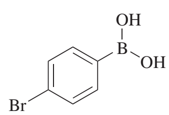
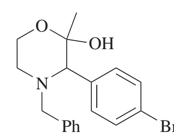
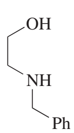
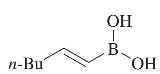
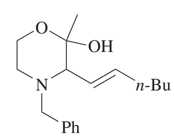
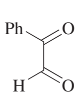
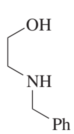
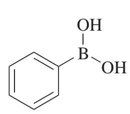
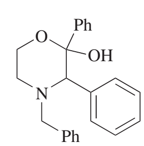
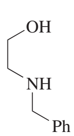
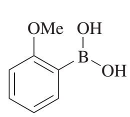
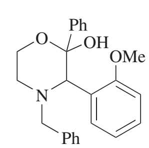
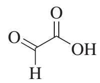
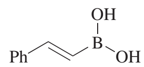
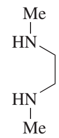
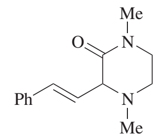
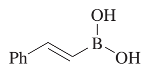
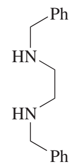
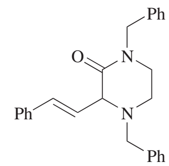
Aldehyde	1,2-Amino Alcohol	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 			Piperidine MW, 110°, 15 min	 (65) dr 100:0	60
			 MW, 110°, 15 min	 (52) dr 100:0	60
			EtOH, rt, 24 h	 (86)[a]	61
			EtOH, rt, 12 h	 +  **I** **II** **I** + **II** (86), **I**/**II** = 93:7	59
			EtOH, rt, 12 h	 +  Ar = 4-BrC_6H_4 **I** **I** + **II** (47), **I**/**II** = 70:30 **II**	59
			EtOH, rt, 12 h	 **I** +  **I** + **II** (75), **I**/**II** = 52:48 **II**	59
			EtOH, rt, 12 h	 +  **I** **II** **I** + **II** (76), **I**/**II** = 86:14	59
			EtOH, rt, 12 h	 **I** +  **I** + **II** (77), **I**/**II** =52:48 **II**	59

TABLE 7C. HETEROCYCLES: 2-HYDROXY AND 2-AMINOMORPHOLINES FROM GLYOXAL AND DERIVATIVES, BORONIC ACIDS, AND 1,2-AMINO ALCOHOLS (*Continued*)

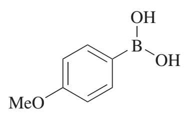
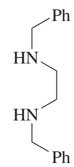
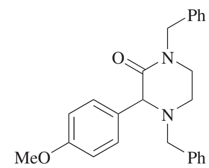
Aldehyde	1,2-Amino Alcohol	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 			EtOH, rt, 12 h	 **I** + **II** (51), **I/II** = —	59
			EtOH, rt, 12 h	 **I** + **II** (66), **I/II** = 90:10	59
			EtOH, rt, 12 h	 **I** + **II** (56), **I/II** = 75:25	59
C_3 			EtOH, rt	 (57) dr 85:15 Time (h): 12 Time (h): 24	59 61
			EtOH, rt, 24 h	 (52) dr 76:24	61
			EtOH, rt	 Time (h) 12 (59) dr 55:45 Time (h) 24 (59) dr 54:46	59 61
C_8 			EtOH, rt	 Time (h) 12 (58) dr 90:10 Time (h) 24 (92) dr 89:11	59 61
			EtOH, rt, 24 h	 (53) dr 83:17	61

[a] The products were a mixture of four diastereoisomers.

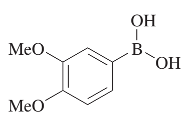
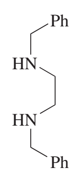
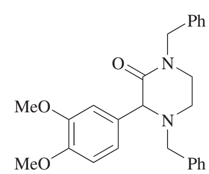
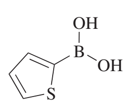
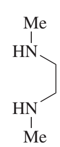
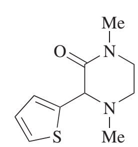
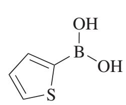
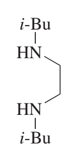
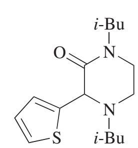
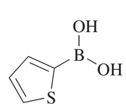
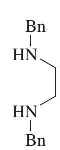
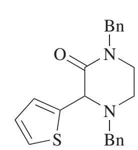
TABLE 7D. HETEROCYCLES: PIPERAZINONES FROM GLYOXYLIC ACID OR ETHYL GLYOXYLATE, ORGANOBORON REAGENTS, AND 1,2-DIAMINES

$CHOCO_2R$	Organoboron	1,2-Diamine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
			MeCN, 80°, 20 h	 (50)	62
			See table.		62

Solvent	Temp	Time (h)	
CH_2Cl_2	rt	24	(73)
MeOH	65°	24	(13)
toluene	110°	2	(75)
MeCN	80°	2	(76)

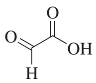
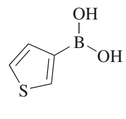
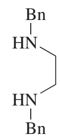
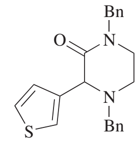
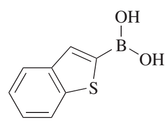
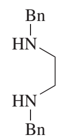
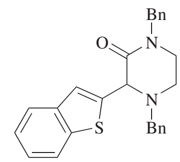
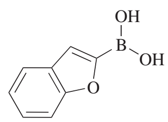
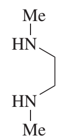
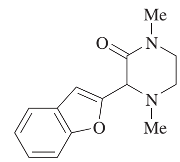
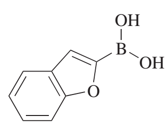
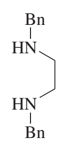
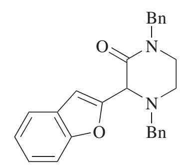
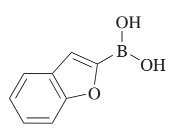
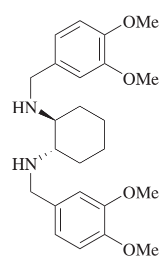
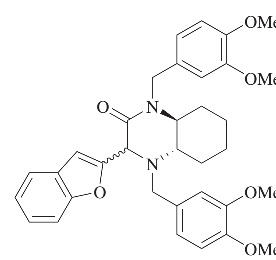
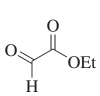
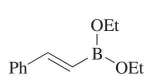
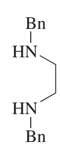
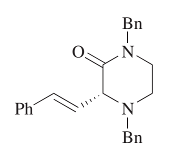
$CHOCO_2R$	Organoboron	1,2-Diamine	Conditions	Product(s) and Yield(s) (%)	Refs.
			See table.		62

Solvent	Temp	Time (h)	
CH_2Cl_2	rt	24	(46)
MeCN	80°	4	(50)
toluene	110°	2	(50)

$CHOCO_2R$	Organoboron	1,2-Diamine	Conditions	Product(s) and Yield(s) (%)	Refs.
			MeCN, 80°, 2 h	 (50)	62
			MeCN, 80°, 24 h	 (48)	62
			MeCN, 80°, 12 h	 (71)	62
			See table.		62

Solvent	Temp	Time (h)	
CH_2Cl_2	rt	24	(45)
EtOAc	rt	24	(28)
MeCN	80°	4	(65)
toluene	110°	2	(42)

TABLE 7D. HETEROCYCLES: PIPERAZINONES FROM GLYOXYLIC ACID OR ETHYL GLYOXYLATE, ORGANOBORON REAGENTS, AND 1,2-DIAMINES (*Continued*)

$CHCO_2R$	Organoboron	1,2-Diamine	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2					
			MeCN, 80°, 24 h	 (35)	62
			THF, 65°, 24 h	 (30)	62
			MeCN, 80°, 3 h	 (80)	62
			MeCN, 80°, 3 h	 (85)	62
			MeCN, 80°, 20 h	 (65) dr 70:30	62
			(*S*)-VAPOL[a] (**4**, 15 mol %), 3 Å MS, toluene, –5°	 (86) er 95:5	38

[a] Please refer to Chart 1 for the structure of (*S*)-VAPOL.

TABLE 7E. HETEROCYCLES: 2-MORPHOLINONES FROM GLYOXYLIC ACID, *N*-SUBSTITUTED PHENYLGLYCINOLS, AND BORONIC ACIDS

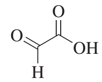
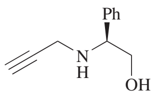
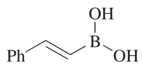
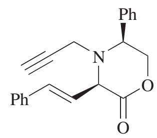
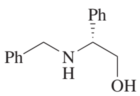
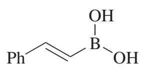
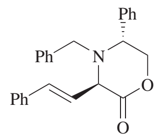
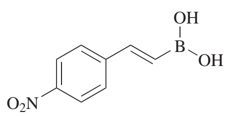
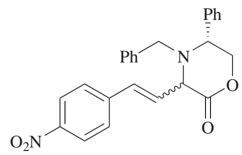
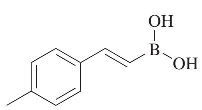
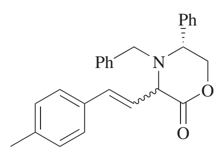
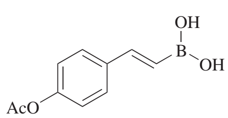
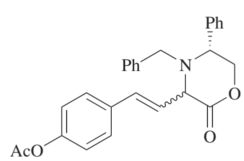
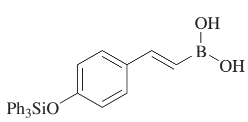
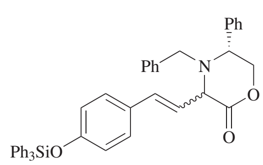
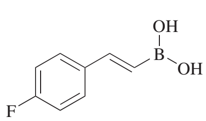
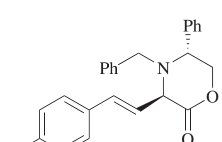
Phenylglycinol	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
*Note: Glyoxylic acid (**I**) is a coreactant in all of the reactions listed in Table 7E.*		 **glyoxylic acid (I)**		
C_{11}				
		Et_3N (*x* eq), CH_2Cl_2, rt	 major *x* / Time (h) / dr: 0 / 12 / (87) / 1.5:1 2 / 24 / (87) / 10:0	36
C_{15}				
 **II**		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 major (89) dr 20:1 1.3:1	34 35
		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 (0)	34
		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 (92) dr 1.3:1	34
		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 (82) dr 1.2:1	34
		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 (90) dr 1:1	34
		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 major (90) dr 3:1	35

TABLE 7E. HETEROCYCLES: 2-MORPHOLINONES FROM GLYOXYLIC ACID, *N*-SUBSTITUTED PHENYLGLYCINOLS, AND BORONIC ACIDS (*Continued*)

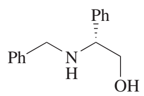
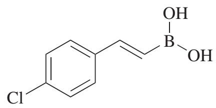
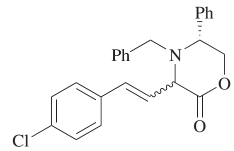
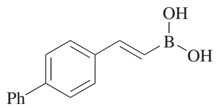
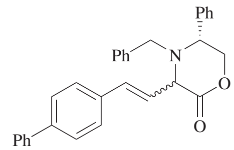
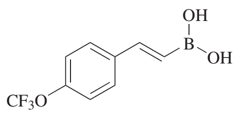
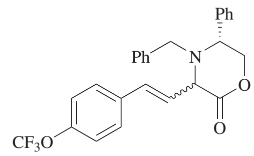
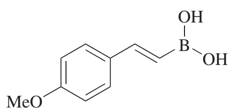
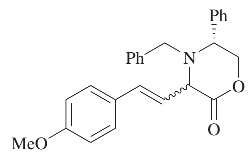
Phenylglycinol	Boronic Acid	Conditions	Product(s) and Yield(s) (%)	Refs.
*Note: Glyoxylic acid (**I**) is a coreactant in all of the reactions listed in Table 7E.*				
C_{15}				
 **II**		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 (95) dr 2.2:1	35
		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 (87) dr 1.4:1	35
		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 (99) dr 1.9:1	35
		1. **I** and **II**, CH_2Cl_2, rt, 10 min 2. Boronic acid, rt, 48 h	 (92) dr 1.1:1	35

TABLE 8. PROPARGYLAMINES FROM SALICYLALDEHYDES AND DERIVATIVES, AMINES, AND POTASSIUM ALKYNYLTRIFLUOROBORATES

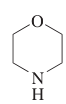
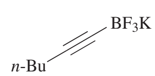
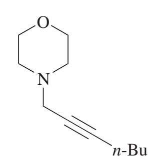
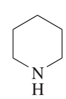
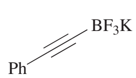
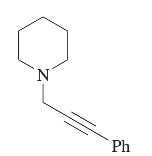
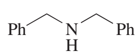
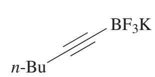
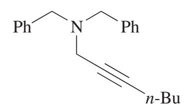
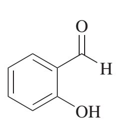
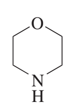
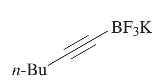
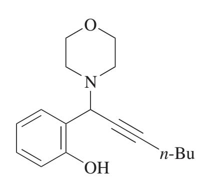
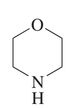
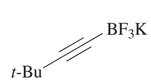
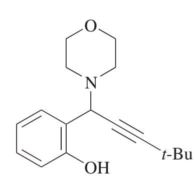
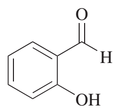
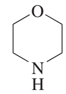
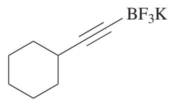
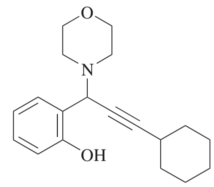
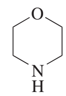
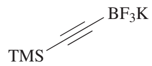
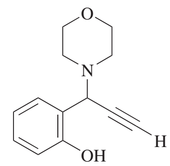
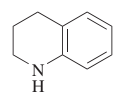
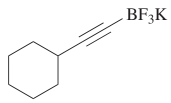
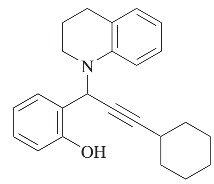
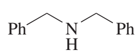
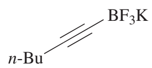
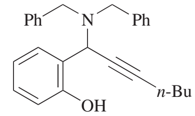
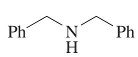
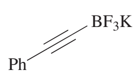
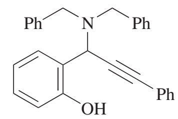
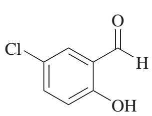
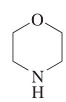
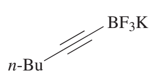
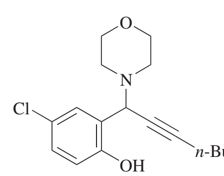
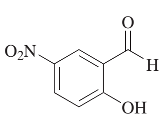
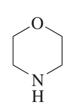
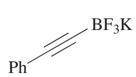
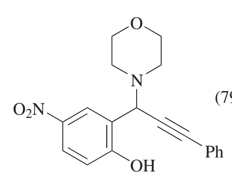
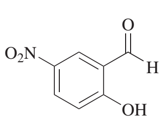
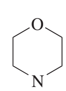
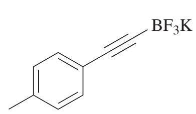
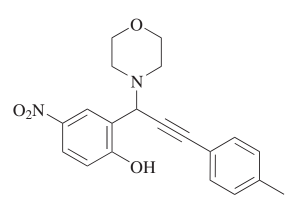
Aldehyde	Amine	RBF_3K	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1					
$(CHO)_n$			$BmimBF_4$, 90°, 4 h	 (90)	63
			$BmimBF_4$, 90°, 4 h	 (83)	63
			$BmimBF_4$, 90°, 4 h	 (92)	63
C_7					
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (76)	63
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (72)	63

TABLE 8. PROPARGYLAMINES FROM SALICYLALDEHYDES AND DERIVATIVES, AMINES, AND POTASSIUM ALKYNYLTRIFLUOROBORATES (*Continued*)

Aldehyde	Amine	RBF_3K	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (78)	63
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (55)	63
			$PhCO_2H$ (1 eq), DMF, 80°, 20 h	 (58)	63
			$PhCO_2H$ (x eq), solvent, 80°, 20 h	 (see below)	63
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (81)	63
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (53)	63
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (79)	63
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (78)	63

x	Solvent	
0	$BmimBF_4$	(10)
1	$BmimBF_4$	(81)
1	BmimBr	(17)
1	$BmimPF_6$	(41)

TABLE 8. PROPARGYLAMINES FROM SALICYLALDEHYDES AND DERIVATIVES, AMINES, AND POTASSIUM ALKYNYLTRIFLUOROBORATES (*Continued*)

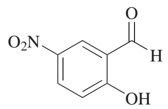
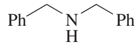
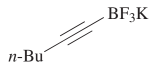
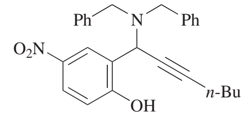
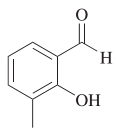
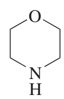
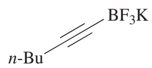
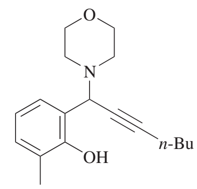
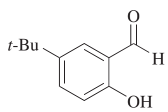
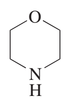
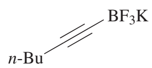
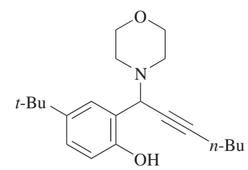
Aldehyde	Amine	RBF_3K	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7					
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (83)	63
C_8					
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (63)	63
C_{11}					
			$PhCO_2H$ (1 eq), $BmimBF_4$, 80°, 20 h	 (76)	63

TABLE 9. ALLYLIC AND HOMOALLYLIC AMINES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS

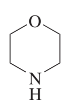
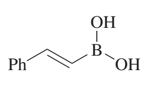
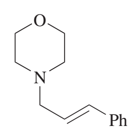
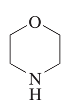
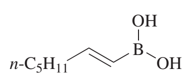
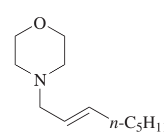
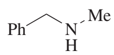
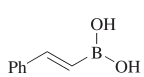
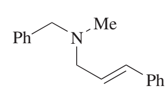
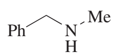
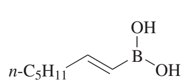
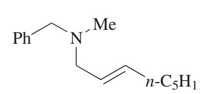
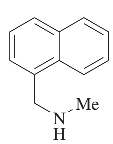
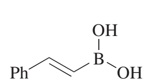
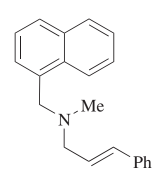
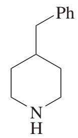
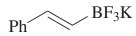
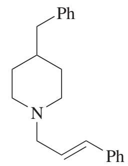
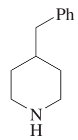
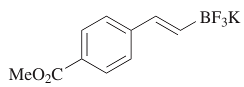
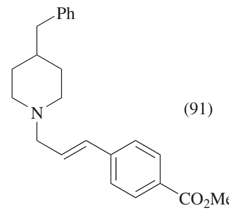
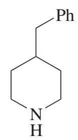
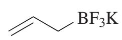
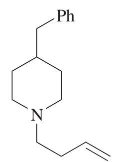
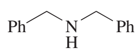
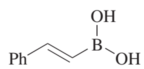
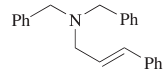
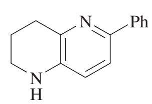
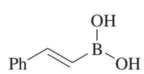
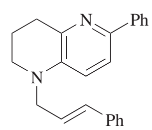
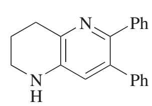
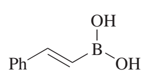
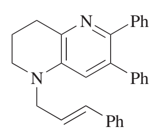
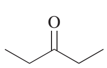
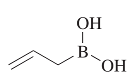
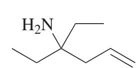
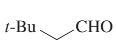
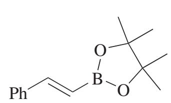
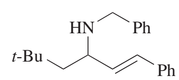
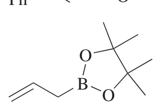
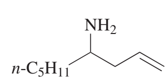
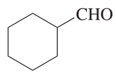
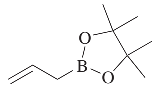
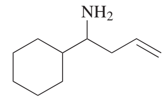
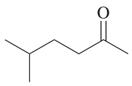
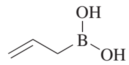
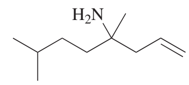
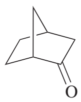
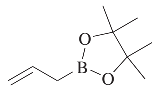
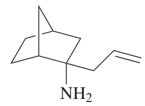
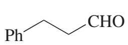
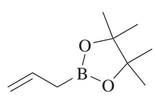
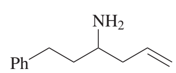
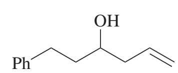
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_1					
$(CHO)_n$			1. $(CHO)_n$, amine, dioxane or toluene, 90°, 10 min 2. Boronic acid, 90°, 30 min; or rt, 3 h	 (89)	7
			1. $(CHO)_n$, amine, dioxane or toluene, 90°, 10 min 2. Boronic acid, 90°, 30 min; or rt, 3 h	 (75)	7
			1. $(CHO)_n$, amine, dioxane or toluene, 90°, 10 min 2. Boronic acid, 90°, 30 min; or rt, 3 h	 (96)	7
			1. $(CHO)_n$, amine, dioxane or toluene, 90°, 10 min 2. Boronic acid, 90°, 30 min; or rt, 3 h	 (84)	7
			1. $(CHO)_n$, amine, dioxane, 90°, 10 min 2. Boronic acid, 90°, 10 min	 (82)	7

TABLE 9. ALLYLIC AND HOMOALLYLIC AMINES FROM ALDEHYDES OR KETONES, AMINES, AND ORGANOBORON REAGENTS (*Continued*)

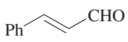
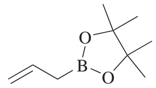
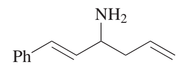
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
$(CHO)_n$	 	1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (90)	48
	 	1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (91)	48
	 	1. $(CHO)_n$, amine, toluene, rt, 10 min 2. Organoboron, BF_3•OEt_2, rt, 5 min; then 90°, 5 h	 (40)	48
	 	1. $(CHO)_n$, amine, dioxane or toluene, 90°, 10 min 2. Boronic acid, 90°, 30 min; or rt, 3 h	 (81)	7
	 	—	 (67) unstable	64
	 	—	 (71) unstable	64
C_5				
	NH_3 	MeOH, rt, 16 h	 (73)	29
C_6				
	 	Solvent, rt	 Solvent / Time (h): MeOH 72 (0); HFIP 4 (0)	21
n-$C_5H_{11}CHO$	NH_3 (25% aq) 	DBSA (10 mol %), rt, 2 h	 (49)	49

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7					
	NH_3		See table.		
	NH_3		MeOH, rt, 16 h	 (85)	29
	NH_3		MeOH, rt, 16 h	 (91) dr 94:6 major (*rac*)	29

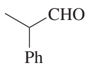
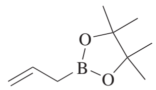
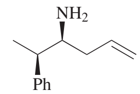
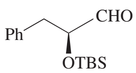
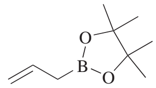
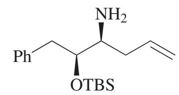
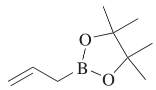
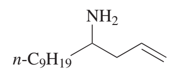
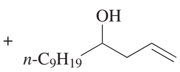
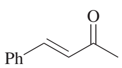
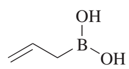
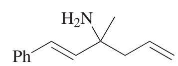
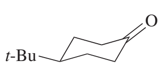
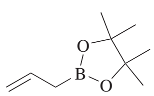
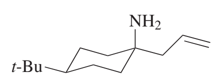
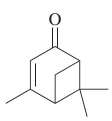
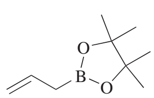
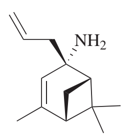
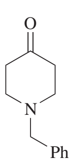
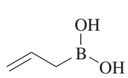
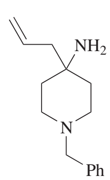
NH_3	Solvent	Additive	Temp	Time (h)		Refs.
liquid	EtOH	—	–78°; then rt	2.5	(80)	28
25% aq	—	DBSA (10 mol %)	rt	6	(68)	49

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_9					
	NH_3		See table.	 **I** +  **II**	

NH_3	Solvent	Additive (mol %)	Temp	Time (h)	I[a]	II[a]	Refs.
liquid	EtOH	—	–78°; then rt	2.5	(78)	(3)	28
25% aq	—	—	rt	2	(34)	(39)	49
25% aq	—	DBSA (10)	rt	2	(72)	(6)	49
25% aq	—	lauric acid (10)	rt	2	(67)	(19)	49
25% aq	—	SDS (10)	rt	2	(56)	(9)	49
25% aq	—	SDBS (10)	rt	2	(72)	(7)	49
25% aq	—	CTAB (10)	rt	2	(44)	(21)	49
25% aq	—	DDMAPS (10)	rt	2	(32)	(14)	49
25% aq	—	Triton X-100[b] (10)	rt	2	(33)	(12)	49
25% aq	—	PEG-400#[c] (10)	rt	2	(44)	(28)	49
25% aq	—	TsOH (10)	rt	2	(25)	(8)	49
25% aq	—	DBSA (5)	rt	2	(69)	(7)	49
25% aq	—	DBSA (20)	rt	2	(65)	(4)	49
25% aq	—	DBSA (50)	rt	2	(42)	(4)	49
25% aq	—	DBSA (10)	rt	4	(72)	(6)	49
25% aq	—	DBSA (10)	rt	6	(86)	(3)	49
25% aq	—	DBSA (10)	rt	12	(84)	(4)	49
liquid	EtOH	—	rt	2	(78)	(3)	49

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_9					
	NH_3		See table.		

NH_3	Solvent	Additive	Temp	Time (h)		Refs.
liquid	EtOH	—	–10°; then rt	5; then 1	(75)	28
25% aq	—	DBSA (10 mol %)	rt	2	(78)	49

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
	NH_3		1. Boronate, NH_3, EtOH, rt, 30 min 2. Aldehyde, rt, 2 h	 major (*rac*) (69) dr 73:27	28
	NH_3		1. Boronate, NH_3, EtOH, –78°; then 0°, 30 min 2. Aldehyde, 0°, 12 h	 major (67) dr 85:15, er 97.5:2.5	28
C_{10}					
n-$C_9H_{19}CHO$	NH_3 (25% aq)		DBSA (10 mol %), rt, 6 h	 (2) +  (52)	49
	NH_3		MeOH, rt, 16 h	 (70)	29
	NH_3		MeOH, rt, 16 h	 major (95) dr 87:13	29
	NH_3		MeOH, rt, 16 h	 major (*rac*) (84) dr 97:3	29
C_{12}					
	NH_3		MeOH, rt, 16 h	 (92)	29

[a] Yields were determined by ^{1}H NMR spectroscopy using 1,2,4,5-tetramethylbenzene as an internal standard.

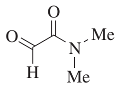
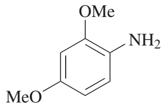
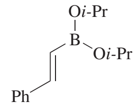
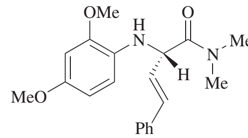
[b] Triton X-100 is polyethylene glycol *tert*-octylphenyl ether.

[c] PEG-400# is polyethylene glycol (MW *ca*. 400).

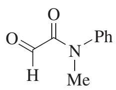
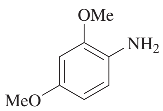
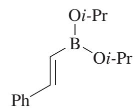
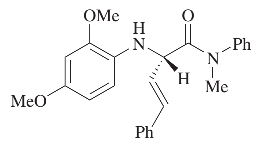
TABLE 10. *N*-ARYL-α-AMIDO AMIDES FROM *N*-ALKYL/ARYL GLYOXYLAMIDES, ANILINES, AND ORGANOBORON REAGENTS

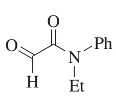
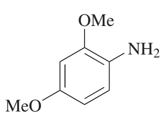
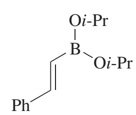
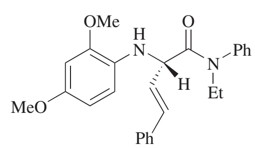
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.

*Please refer to Chart 2 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 			Catalyst (10 mol %), 3 Å MS, toluene, rt, 24 h		114

Catalyst		er[b]
7	(21)[a]	50.5:49.5
8	(22)[a]	65.0:35.0
9	(18)[a]	75.0:25.0
10a	(27)[a]	56.0:44.0
10b	(29)[a]	50.0:50.0
10c	(51)[a]	73.0:27.0
11	(47)[a]	87.0:13.0
12	(27)[a]	50.5:49.5

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 			Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 24 h	 (75)[a] er 93.0:7.0[b]	114

Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 			Cat. **11** (10 mol %), 3 Å MS, solvent, rt, 24 h		114

Solvent		er[b]
toluene	(74)[a]	95.0:5.0
CH_2Cl_2	(71)[a]	81.0:19.0
THF	(8)[a]	79.5:20.5
cyclohexane	(74)[a]	95.0:5.0

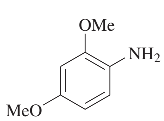
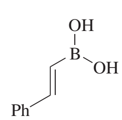
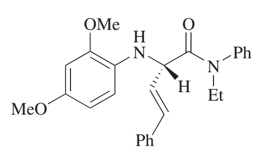
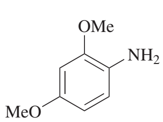
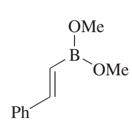
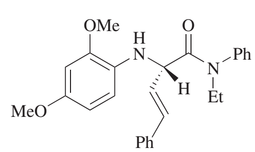
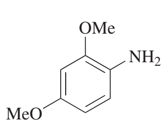
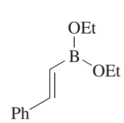
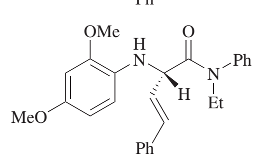
Carbonyl Component	Amine and Organoboron		Conditions	Product(s) and Yield(s) (%)	Refs.
			Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 24 h	 (72)[a] er 88.5:11.5[b]	114
			Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 24 h	 (69)[a] er 94.0:6.0[b]	114
			Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 24 h	 (70)[a] er 94.0:6.0[b]	114

TABLE 10. *N*-ARYL-α-AMIDO AMIDES FROM *N*-ALKYL/ARYL GLYOXYLAMIDES, ANILINES, AND ORGANOBORON REAGENTS (*Continued*)

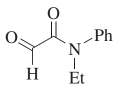
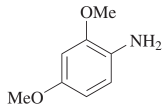
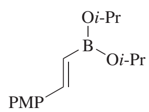
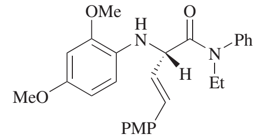
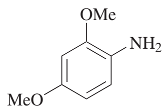
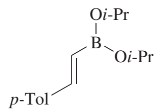
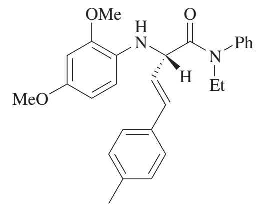
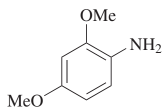
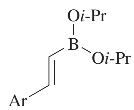
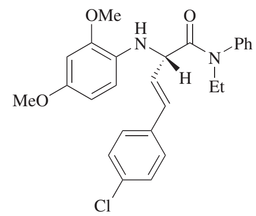
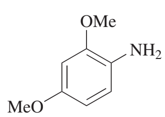
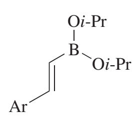
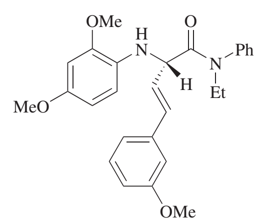
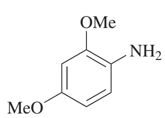
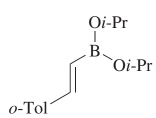
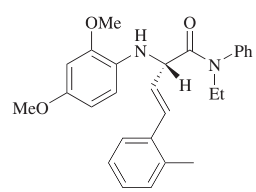
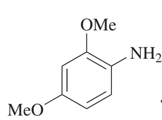
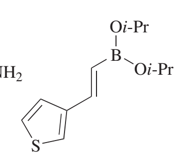
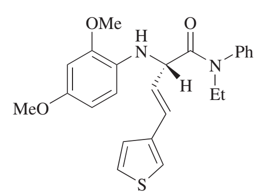
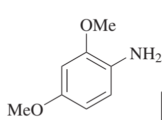
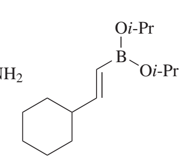
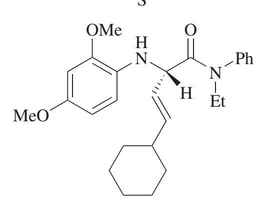
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
*Please refer to Chart 2 preceding the tables for catalyst structures corresponding to the **bold** numbers.*				
C_{10}				
	 	Cat. **11** (10 mol %), 3 Å MS, cyclohexane, rt, 24 h	 (77)[a] er 93.5:6.5[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, cyclohexane, rt, 24 h	 (76)[a] 95.0:5.0[b]	114
	  Ar = 4-ClC_6H_4	Cat. **11** (10 mol %), 3 Å MS, cyclohexane, rt, 24 h	 (65)[a] 95.0:5.0[b]	114
	  Ar = 3-$MeOC_6H_4$	Cat. **11** (10 mol %), 3 Å MS, cyclohexane, rt, 24 h	 (69)[a] 94.5:5.5[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, cyclohexane, rt, 24 h	 (86)[a] er 96.5:3.5[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, cyclohexane, rt, 24 h	 (77)[a] er 94.5:5.5[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, cyclohexane, rt, 24 h	 (53)[a] er 90.0:10.0[b]	114

TABLE 10. *N*-ARYL-α-AMIDO AMIDES FROM *N*-ALKYL/ARYL GLYOXYLAMIDES, ANILINES, AND ORGANOBORON REAGENTS (*Continued*)

Please refer to Chart 2 preceding the tables for catalyst structures corresponding to the ***bold*** *numbers.*

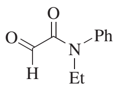
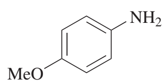
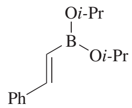
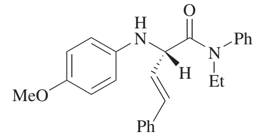
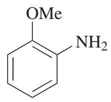
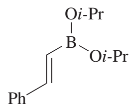
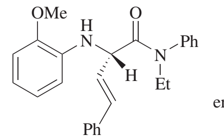
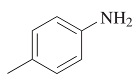
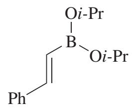
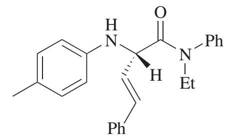
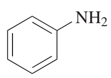
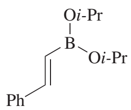
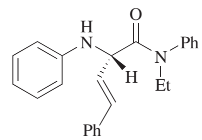
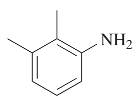
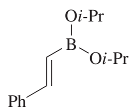
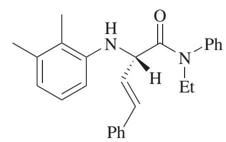
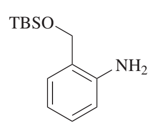
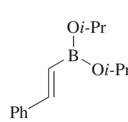
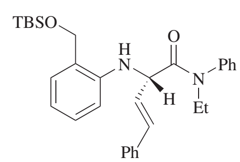
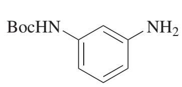
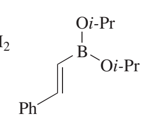
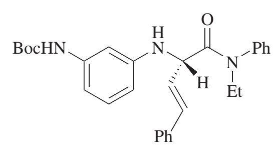
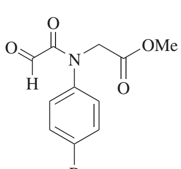
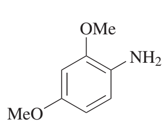
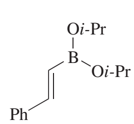
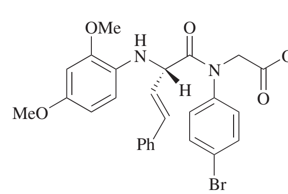
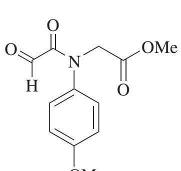
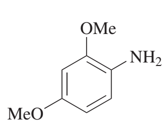
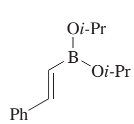
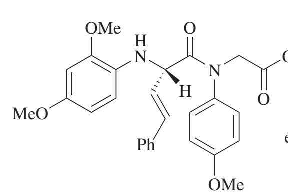
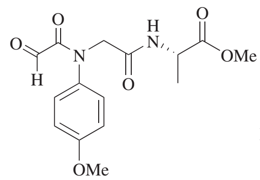
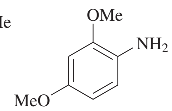
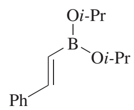
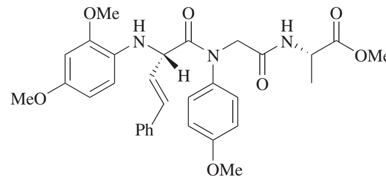
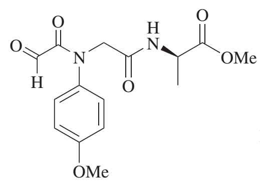
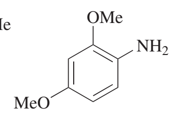
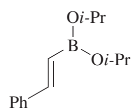
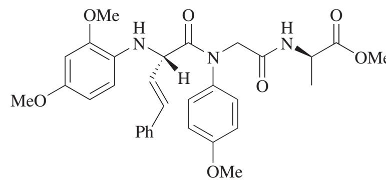
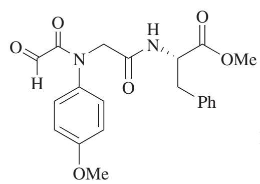
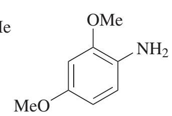
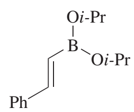
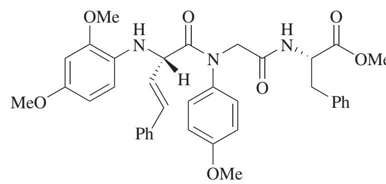
Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (62)[a] er 91.0:9.0[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (77)[a] er 93.0:7.0[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (78)[a] er 93.5:6.5[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (58)[a] er 92.0:8.0[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (56)[a] er 95.0:5.0[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (63)[a] er 91.0:9.0[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, cyclohexane, rt, 72 h	 (54)[a] er 95.0:5.0[b]	114
	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (71)[a] er 96.0:4.0[b]	114
C_{11} 	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (67)[a] er 91.0:9.0[b]	114

TABLE 10. *N*-ARYL-α-AMIDO AMIDES FROM *N*-ALKYL/ARYL GLYOXYLAMIDES, ANILINES, AND ORGANOBORON REAGENTS (*Continued*)

Carbonyl Component	Amine and Organoboron	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (58)[a] dr 85:15[c]	114
	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (57)[a] dr 89:11[c]	114
C_{20} 	 	Cat. **11** (10 mol %), 3 Å MS, toluene, rt, 48 h	 (60)[a] dr 88:12[c]	114

*Please refer to Chart 2 preceding the tables for catalyst structures corresponding to the **bold** numbers.*

[a] The yield of isolated product for the two step process is based on the carbonyl component.

[b] The enantiomeric ratio was determined by chiral HPLC analysis.

[c] The diastereomeric ratio was determined by ^{1}H NMR analysis.

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